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# JOURNAL

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## THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART I.

#### Organic Chemistry.

**Ethane and Propane.** By L. MEYER (*Ber.*, 1894, 27, 2767—2769; compare Abstr., 1893, i, 681).—The following physical constants of ethane and propane have been accurately determined.

Density of the liquid—

Temperature . . . .	0°.	+6.2°.	10.5°.	11.5°.	15.9°.
Density { ethane..	0.466	—	0.396	—	—
{ propane	0.536	0.524	—	0.520	0.515

#### *Vapour Pressure.*

Temp.	Pressure in atmospheres.		Temp.	Pressure in atmospheres.	
	Ethane.	Propane.		Ethane.	Propane.
—89.5°	0.95	—	0°	23.3	—
—37	—	1.0	+1	—	5.1
—33	—	1.8	5.5	—	5.9
—31	11.0	—	12.5	—	7.1
—20	14.5	—	15	32.3	—
—19	—	2.7	22	—	9.0
—15	—	3.1	34.5	50.0	—
—11	18.3	3.6	53	—	17.0
— 5	—	4.1	85	—	35.0
— 2	—	4.8	102	—	48.5





higher boiling portion of the product of the action of chlorine on trimethylene yields three compounds on further fractionation. These are trimethylenic chloride,  $C_3H_6Cl_2$ , boiling at  $119-120^\circ$ ,  $\beta$ -chloropropylidene chloride, boiling at  $146-148^\circ$ , and trichlorhydrin, boiling at  $155-157^\circ$ , the last of these being only present in very small quantity.

A. H.

**Constitution of Salts of the Nitro-paraffins.** By J. U. NEF (*Annalen*, 1894, **280**, 263—291).—The result of the author's experiments is to show that sodium nitroethane must be represented by the expression  $CHMe\cdot NO\cdot ONa$ , and not by the formula  $CHMeNa\cdot NO_2$ ; the addition of sodium ethoxide and subsequent elimination of water involved in its formation being comparable with the formation of ethylic sodiomalonate from ethylic malonate and sodium ethoxide. In support of this conclusion, the following is brought forward.

The free nitro-paraffins do not correspond in constitution with their salts; this is shown by the difficulty experienced in regenerating them from the salts by the action of acids. When a 10 per cent. solution of sodium nitroethane is quickly added to 20 per cent. sulphuric acid, a green coloration is produced, and heat is developed, accompanied by the liberation of acetaldehyde and nitrous oxide. Regeneration of nitroethane takes place only when dilute sulphuric acid is slowly added to a well-cooled solution of nitroethane in slight excess of caustic potash or sodium ethoxide, and even under these conditions the yield does not exceed 25 per cent. Similarly, nitroethane mercurichloride yields acetaldehyde and nitrous oxide, but no trace of nitroethane, when treated with acids; this observation is directly opposed to V. Meyer's statement that nitroethane is liberated from the mercuric salt by acids. The addition of dilute sulphuric or hydrochloric acid to the aqueous solution of sodium nitromethane gives rise to nitrous oxide, formaldehyde, nitrous acid, carbonic anhydride, and hydroxylamine; by keeping the temperature low, and adding the acid very slowly, about 25 per cent. of nitromethane may be recovered. The sodium salt of secondary nitropropane undergoes an analogous decomposition with formation of acetone and nitrous oxide.

The formation of a yellow, explosive mercuric salt, on adding sodium nitromethane to mercuric chloride solution, has been observed by V. Meyer and Rilliet (*Ber.*, **5**, 1030), who regarded it as mercuric nitromethane, but did not investigate it further. Analysis shows it to be free from hydrogen. The white precipitate, which is first formed on mixing the solutions, consists most probably of the unstable mercuric nitromethane, and this, immediately losing water, becomes converted into mercuric fulminate, which may be obtained in quantities amounting to 20 per cent. of the sodium nitromethane employed. There is every probability that the yellow precipitate described by V. Meyer and Rilliet consists of *basic mercuric oximido-carbonate*,  $(Hg\langle\overset{O}{\underset{O}{>}}C:NO)_2Hg$ , which forms an insoluble residue

from which the solution of mercuric fulminate may be filtered. The salt explodes very readily, but may be cautiously dried at  $100^\circ$ ; it is

unchanged by dilute nitric or sulphuric acid, but with hydrochloric acid, it yields mercuric chloride, carbonic oxide, and a substance having the odour of hydrogen cyanide. It is decomposed by strong hydrochloric acid into carbonic anhydride and hydroxylamine.

Dinitroethane is best prepared by agitating for 24 hours a mixture of 50 grams of bromonitroethane, 50 c.c. of alcohol, and 56 grams of potassium nitrite dissolved in 56 c.c. of water; potassium dinitroethane separates out slowly, and may be converted into the silver salt by mixing its solution with silver nitrate. When silver dinitroethane is allowed to fall into twice its weight of methylic iodide, silver iodide is at once precipitated, and the odour of formaldehyde becomes perceptible (compare Duden, Abstr., 1894, i, 101). By suitable treatment, the liquid may be made to yield dinitroethane, ethylnitrolic acid,  $\beta$ -dinitropropane, and an oil which is most probably the ethylic salt of ethylnitrolic acid. The *benzoic* derivative of this acid forms colourless needles which melt at  $135^{\circ}$ . Silver dinitromethane is also decomposed when thrown into five parts of ethylic iodide, acetaldehyde, ethylnitrolic acid, dinitroethane, and an oil, which is most probably  $\beta$ -dinitrobutane, being formed.

M. O. F.

**Oil of Pelargonium from Reunion.** By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 1894, **119**, 281—284).—When crude oil of pelargonium from Reunion is saponified with alcoholic potash and then fractionated, the principal fraction boiling at  $115\text{--}116^{\circ}$  is a colourless oil with an odour of roses; sp. gr. at  $0^{\circ} = 0.8866$ ; observed rotation in column 200 mm. long =  $-12^{\circ} 28'$ . The authors call it provisionally *pelargonium rhodinol*; with acetic anhydride, it yields an *acetate* which boils at  $120^{\circ}$  under a pressure of 10 mm., and which, when saponified, regenerates rhodinol with a somewhat lower sp. gr., 0.8826, and a rotatory power of  $-7^{\circ} 12'$ . This substance is under investigation.

The fraction boiling at  $80\text{--}100^{\circ}$  closely resembles licareol. When treated with acetic anhydride, it yields a considerable proportion of a hydrocarbon boiling at  $60\text{--}80^{\circ}$  in a vacuum, and an acetate boiling at about  $120^{\circ}$ ; but about half the product is unchanged even in presence of excess of acetic anhydride, and this portion, boiling at  $90\text{--}95^{\circ}$ , is a mixture of two ketones, one saturated and identical or isomeric with menthone,  $C_{10}H_{18}O$ , and the other,  $C_{10}H_{16}O$ , unsaturated. The constitution of the latter has not yet been ascertained, but the mixture of the two, when oxidised, yields large quantities of acetone, and of  $\beta$ -methyladipic acid melting at  $84^{\circ}$ . The alcohol which accompanies these ketones is licareol, and the alcohol regenerated from the acetate is identical with licarhodol.

The acids present in the crude oil of pelargonium as ethereal salts are acetic, isobutyric, isovaleric, and tiglic acids, and a small quantity of an acid, probably  $C_9H_{15}\cdot COOH$ , boiling at  $250^{\circ}$ .

There is also present a dark blue liquid which boils at about  $165\text{--}170^{\circ}$  under a pressure of 10 mm., and seems to be the ether  $(C_{10}H_{17})_2O$ ; a small quantity of a substance resembling the stearoptene of roses is likewise present.

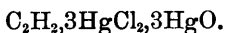
C. H. B.

**Acetol Ethyl Ether and the Formation of Epiethylin.** By A. PERATONER (*Gazzetta*, 1894, **24**, ii, 36—44).—The author has not obtained satisfactory results in the preparation of acetol ethyl ether,  $\text{CH}_2\text{Ac}\cdot\text{OEt}$ , by using Erlenbach's method (*Abstr.*, 1892, 953); the hydrogen chloride liberated during the distillation acts on the product. On turning to Kutscheroff's process, namely, the action of freshly prepared mercuric bromide on ethylic ethylpropargylate suspended in water, it was found that when the ethylic salt was treated with an excess of somewhat impure mercuric bromide in presence of water, violent ebullition occurred, and ethylic alcohol was the only product which could be isolated; on using less mercuric bromide and warming on the water bath, ethyl glycidic ether (epiethylin) was obtained. The latter has the normal molecular weight in boiling acetic acid, and was identified by its boiling point and by its yielding ethyl chlorhydrin when dissolved in hydrochloric acid. The author is unable to say what impurity in the mercuric bromide caused the action to proceed in the way mentioned above.

Acetol ethyl ether is best prepared by agitating ethylic ethylpropargylate with a saturated solution of mercuric chloride; a white substance,  $2\text{C}_5\text{H}_8\text{O}_2\cdot 3\text{HgCl}_2\cdot 3\text{HgO}$ , falls, and yields the ether on distillation with hydrochloric acid and subsequent treatment of the distillate with sodium carbonate. With sodium hydrogen sulphite, the ether yields a compound,  $\text{C}_5\text{H}_{10}\text{O}_2\cdot\text{NaHSO}_3$ , crystallising in long, prismatic needles. The oxime of the ether,  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}$ , is obtained as an oil boiling at  $185\text{--}190^\circ$ ; the acetoxime boils at  $188^\circ$ , has an odour much resembling that of acetoxime, and is hydrolysed by heating with dilute hydrochloric acid.

Acetol ethyl ether boils at  $129^\circ$  under 759.5 mm. pressure (corr.), and has the sp. gr. 0.9562 at  $0^\circ$  and 0.8497 at  $99.97^\circ$ . Ethyl glycidic ether boils at  $128^\circ$  under 760 mm. pressure, and has the sp. gr. 0.9635 at  $0^\circ$  and 0.8277 at  $99.97^\circ$ .

Acetylene forms a mercuric compound of the composition



W. J. P.

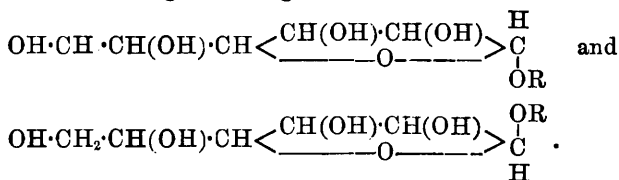
**The Second Methylglucoside.** By W. A. VAN ECKENSTEIN (*Rec. Trav. Chim.*, 1894, **13**, 183—186).—When preparing methylglucoside by E. Fischer's method (*Abstr.*, 1894, i, 4), the author noticed that the rotatory power of the hydrochloric acid solution increased, and he was thus led to suspect the presence in this solution of a lævorotatory methylglucoside, which was gradually undergoing a transformation into the dextrorotatory variety. By using a more dilute (28 per cent.) solution of hydrogen chloride in methylic alcohol, and acting with this on glucose, the acid being neutralised as soon as the solution ceased to reduce Fehling's solution, he obtained a mixture of the two isomeric methylglucosides in about equal proportions, and on crystallising this mixture he found that the lævorotatory methylglucoside was first deposited. This crystallises in octahedra, which contain  $\frac{1}{2}\text{H}_2\text{O}$ ; melts when anhydrous at  $104^\circ$ ; is more soluble in alcohol and less so in water than its dextrorotatory isomeride, and is much more readily hydrolysed by acids.

C. F. B.

**Influence of Configuration on the Action of Enzymes.** By E. FISCHER (*Ber.*, 1894, **27**, 2985—2993).—Fischer and Thierfelder (*Abstr.*, 1894, i, 486) put forward the hypothesis that the active chemical agents of the yeast cells can only attack those sugars which have a similar configuration. The present experiments show that the action of the two enzymes, invertase and emulsin, on these substances is likewise dependent on the molecular configurations of the compounds dealt with.

*Invertase.*—The experiments with this enzyme were made with the filtered extract obtained by digesting 1 part of air-dried beer-yeast (Frohberg type) with 15 parts of water for 15 hours at 30—35°.

The formula proposed by the author for the glucosides of the alcohols (*Abstr.*, 1894, i, 4) renders possible the existence of two stereoisomerides having the configurations



The second modification of methylglucoside may be obtained from the syrupy mother liquor from the already-known modification (*loc. cit.*). The author has been forestalled, however, in its isolation, by van Ekenstein (preceding abstract). He proposes to call the methylglucoside previously described the  $\alpha$ -modification, and the newly-discovered isomeride the  $\beta$ -modification.

When  $\alpha$ -methylglucoside is treated with invertase at 30—35°, about half is hydrolysed at the end of 20 hours, whilst the  $\beta$ -modification remains unaltered under these circumstances. This fact is the more remarkable, seeing that van Ekenstein has observed that the  $\beta$ -modification is more readily hydrolysed by dilute acids than the  $\alpha$ -modification. Crystallised ethylglucoside (*Abstr.*, 1894, i, 565) is hydrolysed by invertase, and therefore belongs probably to the  $\alpha$ -series. Benzyl- and glyceryl-glucosides have, as yet, only been obtained in the amorphous condition, but inasmuch as they are hydrolysed much less completely than the pure  $\alpha$ -glucoside, they are probably mixtures of the  $\alpha$ - and  $\beta$ -modifications. Methyl- and ethyl-galactosides, methyl-, ethyl-, and benzyl-arabinosides, and methyl- and ethyl-rhamnosides are not attacked by invertase: the five first compounds are crystalline, and are probably the  $\beta$ -modifications. Methyl-*l*-glucoside, probably the  $\alpha$ -modification, was obtained as a syrup; the action of invertase gave a negative result.

The author finds that yeast extract readily and completely effects the conversion of maltose into glucose, although commercial solid invertase is without action on this sugar, as it is, also, on  $\alpha$ -methylglucoside. Whether the enzyme which effects this change is identical with the so-called glucase of maize cannot, at present, be ascertained. Contrary to Dastre's observation (*Compt. rend.*, **96**, 932), the enzyme of yeast is without action on milk sugar. The author, there-

fore, regards maltose and milk sugar as related to one another in the same way as methylglucoside is to methylgalactoside.

Inulin and starch are not hydrolysed by invertase, neither are salicin, coniferin, phloridzin, or Michael's synthetical phenolglucoside (*Compt. rend.*, **89**, 355). A solution of invertase hydrolyses amygdalin readily with the formation of glucose, but neither benzaldehyde nor hydrogen cyanide are produced, so that its action is quite different from that of emulsin.

Invertase solution rapidly undergoes putrefactive change, but this may be prevented by the addition of chloroform, which does not influence its hydrolytic action. An addition of  $2\frac{1}{2}$  per cent. of phenol, however, completely arrests the action of invertase. The extract obtained from yeast of the Saaz type behaves in the same way towards the glucosides of the alcohols and maltose as that from the Froberg type. The enzyme from milk-sugar yeast does not, however, hydrolyse maltose, and the same is to be expected of *Saccharomyces exiguus Ludwigii* or *apiculatus*.

*Emulsin*.—The experiments were carried out at 30–35°, with 1 part of this enzyme to 2 parts of the glucoside and 20 parts of water, the action being maintained for 15–20 hours. Amongst the glucosides of the alcohols, only the derivatives of *d*-glucose appear to be hydrolysed by emulsin, but in contradistinction to the action of invertase,  $\beta$ -methylglucoside, and not the  $\alpha$ -modification, is hydrolysed. Maltose and saccharose are not appreciably attacked by emulsin, although this enzyme hydrolyses milk sugar.

*Enzyme of Kephir grains*.—The author was unable to test the action of the enzyme of milk-sugar yeast on milk sugar itself on account of lack of this yeast. He finds, however, that an aqueous extract of kefir grains hydrolyses milk sugar.

The paper concludes with a theoretical discussion on the influence of the geometrical configuration of glucosides on the action of enzymes.

A. R. L.

**Maltose and its Anhydride.** By C. A. LOBRY DE BRUYN and F. H. VAN LEENT (*Rec. Trav. Chim.*, 1894, **13**, 218–222).—Maltose loses 1 mol. of water and forms an anhydride when it is heated at 130–135°, or in a vacuum at 105°, or when it is boiled with absolute alcohol. The anhydride readily absorbs water, maltose being re-formed; its specific rotation  $\alpha_D = 140.7^\circ$ , but after 24 hours it becomes  $137.7^\circ$ ; it yields the same phenylosazone as maltose itself.

C. F. B.

**Formation of Pentosans in Plants.** By G. DE CHALMOT (*Ber.*, 1894, **27**, 2722–2725).—Pentoses are not direct products of the process of assimilation in plants, and, therefore, must be formed from hexoses. Now xylosans are always associated with celluloses containing glucose-groups, and arabinose with substances containing galactose-groups. And if E. Fischer's stereometric formulæ of *d*-glucose and *d*-galactose be compared with those of *l*-xylose and *l*-arabinose, it will be seen that the two latter can be derived respectively from the two former by oxidising the end group,  $\text{CH}_2\cdot\text{OH}$ , which these contain, and replacing it by H. For this it would be necessary that the  $\text{CHO}$ -group should be protected from oxidation, as might be the case if the

molecule had formed condensation products with other molecules. And so it seems probable that complex molecules containing pentose-groups are formed by the oxidation of complex molecules containing hexose-groups.

C. F. B.

**Properties and Reactions of Pectous Substances.** By L. MANGIN (*Bied. Centr.*, 1894, **23**, 547—548; from *Jour. de Bot.*, 1892, 206, 235, and 363).—Pectous substances are divided into: (1) Pectose, which occurs with cellulose, and is insoluble in water and in copper ammonium hydroxide, but is dissolved by alkalis. (2) Pectin, which readily gelatinises in water and is not precipitated by lead acetate. (3) Parapectin, obtained by prolonged boiling from pectin; it is precipitated by lead acetate. (4) Metapectin, produced by boiling parapectin with dilute acids; it is precipitated by barium chloride. (5) Pectic acid, insoluble in water, alcohol, and acids; the alkaline salts are soluble, but not those of the alkaline earths. The acid is also soluble in alkaline carbonates and phosphates, and in the ammonium salts of organic acids, forming, it is supposed, double salts. When the acid is boiled with alkalis, metapectin (? metapectic acid) is formed. This is quite insoluble in water, and forms soluble salts with all bases, including calcium and barium. The metapectates become yellow in presence of an excess of alkali. Metapectic acid is converted by sulphuric acid into arabinose and another substance not further examined.

Pectous substances yield mucic acid when heated with dilute nitric acid. They are not coloured blue or violet by iodine. They occur in all plants (except some fungi), and in all membranes except those which have become woody.

N. H. M.

**Selenitines.** By G. CARRARA (*Gazzetta*, 1894, **24**, ii, 173—179).—The author has succeeded in preparing a new class of selenium compounds, to which he gives the name selenitines; they are thetines, in which selenium takes the place of sulphur.

*Diethylselenitine bromide*,  $\text{SeEt}_2\text{Br}\cdot\text{CH}_2\cdot\text{COOH}$ , is prepared by warming ethylic selenide with fused bromoacetic acid; the action is complete in a day, and the bromide is obtained in deliquescent prisms, melting at  $74^\circ$ . It is soluble in water or alcohol, but insoluble in ether, and has an acid reaction. *Diethylselenitine platinochloride*,  $(\text{C}_2\text{H}_5\text{O}_2\text{Se})_2\cdot\text{H}_2\text{PtCl}_6$ , may be prepared by a process similar to that used in preparing the platinochlorides of the thetines (*Abstr.*, 1893, i, 633); it is crystalline, and melts and decomposes at  $150$ — $151^\circ$ . The corresponding *hydroxide*,  $\text{OH}\cdot\text{SeEt}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained by the action of moist silver oxide on the bromide; it is a deliquescent, crystalline substance, having an acid reaction.

On treating the dibromide of diethyl selenide,  $\text{SeEt}_2\text{Br}_2$ , with sufficient silver acetate to eliminate one-half of the bromine, and evaporating the solution, a product is obtained, consisting of white, deliquescent needles. This, after treatment with silver chloride, yields, with platinic chloride, the *ethylic platinochloride* of diethyl selenide,  $(\text{SeEt}_2)_2\cdot\text{Et}_2\text{PtCl}_6$ . The corresponding *methylic platinochloride*,  $(\text{SeEt}_2)_2\cdot\text{Me}_2\text{PtCl}_6$ , crystallises in laminae.

W. J. P.

**Mercuric Formamide.** By B. FISCHER and B. GRÜTZNER (*Arch. Pharm.*, 1894, **232**, 329—333).—Recently prepared mercuric oxide dissolves in formamide, and, on treatment with alcohol, *basic mercuric formamide*,  $\text{HCO}\cdot\text{NH}\cdot\text{Hg}\cdot\text{OH}$ , is precipitated; it is a colourless powder, which is decomposed when heated above  $35^\circ$ , and at ordinary temperatures by the action of light; it dissolves in dilute hydrochloric acid and in formamide, and is decomposed when heated with potash, ammonia being evolved; the mercury is only incompletely precipitated by hydrogen sulphide. By the action of hydrochloric acid on the preceding compound, the *chlorides*,  $(\text{HCO}\cdot\text{NH}\cdot\text{HgCl})_2\cdot 3\text{HCl}$  and  $\text{HCO}\cdot\text{NH}\cdot\text{HgCl}$ ,  $\text{HCl}$ , are formed, the former with dilute, the latter with concentrated, acid; both are crystalline, have an acid reaction, and precipitate albumin, but cease to do so and become neutral by treatment with sodium chloride. With potash, the former, which is the more soluble, gives a pale yellow, the latter a greyish-yellow precipitate, and, on boiling, ammonia is evolved.

J. B. T.

**Bivalent Carbon.** By J. U. NEF (*Annalen*, 1894, **280**, 291—342; compare *Abstr.*, 1892, 1438).—The author has accumulated more evidence in support of his opinion that isocyanides contain bivalent carbon, having studied methylic and ethylic isocyanides on the lines already indicated in the investigation of the analogous aromatic compounds.

*Methylimidobenzoylformic acid*,  $\text{NMe}\cdot\text{CBz}\cdot\text{OH}$ , is obtained by heating a mixture of methylic isocyanide with benzoic chloride, in molecular proportion, for half an hour at  $100^\circ$ ; it forms heavy, pale yellow crystals, which melt at  $74^\circ$ . The solution in dilute caustic soda yields an oily hydrate when acidified, together with what is probably a polymeric modification of the original substance. The *phenylhydrazone hydrate* is produced by combination with phenylhydrazine in ethereal solution; it is insoluble in water, and is not decomposed by cold caustic soda, but, when warmed for half an hour with the latter, methylamine is eliminated, and the phenylhydrazone of benzoylformic acid formed; this melts at  $163^\circ$  (Elbers found  $153^\circ$ ).

Ethylic isocyanide undergoes molecular rearrangement when heated for three hours at  $230$ — $255^\circ$ , propionitrile being formed almost quantitatively. Heated for two hours at  $110$ — $120^\circ$  with sulphur dissolved in carbon bisulphide, it is converted into ethylthiocarbimide.

*Ethylimidothioformic acid*,  $\text{NEt}\cdot\text{CH}\cdot\text{SH}$ , is prepared by heating, for four hours at  $100^\circ$ , a mixture of ethylic isocyanide and alcohol saturated with hydrogen sulphide. It is a yellow oil, which boils at  $125^\circ$  (14 mm.); its taste is bitter, and it dissolves in water slowly, but is more readily soluble in dilute caustic soda.

*Isocyanoethylic dichloride* (*ethylimidocarbonyl chloride*),  $\text{NEt}\cdot\text{CCl}_2$ , is produced on passing chlorine over the surface of a solution of ethylic isocyanide in chloroform kept at  $-19^\circ$ ; a better method of preparation consists in adding sulphuryl chloride to a solution of ethylic isocyanide in ether at  $-15^\circ$ . It is a colourless oil, which boils at  $102^\circ$ .

*Ethylimidopyruvic phenylhydrazone*,  $\text{NEt}\cdot\text{C}(\text{OH})\text{CMe}\cdot\text{N}\cdot\text{NHPh}$ , is obtained by the interaction of ethylic isocyanide and acetic chloride; the product, after remaining for 12 hours at the ordinary temperature,

is mixed with water at  $0^{\circ}$  and treated with phenylhydrazine. The hydrazone melts at  $165^{\circ}$ , and is insoluble in water and alkalis. If, previous to decomposition with water, the product be distilled under 15 mm. pressure, a yellow oil passes over at  $50-60^{\circ}$ , the boiling point of which is  $100-130^{\circ}$  at atmospheric pressure. It consists of *ethyl-imidopyruvic chloride*,  $\text{NEt}:\text{CCl}:\text{COMe}$ , but, as it undergoes partial decomposition when boiled, it could not be obtained pure. The ease with which this and many additive compounds of the isocyanides undergo dissociation, coupled with the violent character of the action during their formation from the constituents, suggests a parallel between bivalent carbon compounds and those of trivalent nitrogen.

Carbonyl chloride unites with ethylic isocyanide at  $-15^{\circ}$  with explosive violence, which is somewhat moderated by the employment of ether as a diluent; the product, however, decomposes when boiled at reduced pressure, and was not further investigated. Ethylic chlorocarbonate forms an additive compound, which dissociates at  $100^{\circ}$  into carbonic anhydride, ethylic chloride, and ethylic isocyanide, the latter at once becoming polymerised. That the intermediate imidochloride,  $\text{NEt}:\text{CCl}:\text{COOEt}$ , is first formed, is shown by the production of ethylic oxamate when the crude product is warmed with lime-water, after polymerised ethylic isocyanide and the ether employed in the operation have been removed.

From the foregoing experiments, it will be seen that the aliphatic isocyanides differ from those of the aromatic series only in their greater chemical activity. In addition to the substances already mentioned, ethylic isocyanide reacts with carbon tetrachloride at  $180^{\circ}$ , with benzenesulphonic chloride at  $85^{\circ}$ , and with benzylic chloride at  $120^{\circ}$ , but the products do not invite further investigation. It is remarkable that ethylic isocyanide and sodium ethoxide may be heated together for an hour at  $130-170^{\circ}$  without action taking place.

The author advances the view that fulminic acid contains bivalent carbon, and is to be represented by the formula  $\text{C}:\text{NOH}$ . This is rendered probable by the synthesis of mercuric fulminate from sodium nitromethane (this vol., i, 3), and further light is thrown on the question by the contradiction of the statement that hydrogen cyanide is formed when fulminates are decomposed by hydrochloric acid. If this acid, mixed with the same volume of water, is added to the aqueous solution of sodium fulminate at  $0^{\circ}$ , and the mixture at once extracted with ether, an ethereal solution of *chloro-formoxime*,  $\text{CHCl}:\text{NOH}$ , is obtained, and on cautious removal of the solvent at  $0^{\circ}$ , the substance is deposited in long, transparent, colourless needles; it is also formed when silver fulminate is added to hydrochloric acid at  $0^{\circ}$ . The substance, in the solid state and also in concentrated ethereal solution, remains unchanged at  $0^{\circ}$ , but it spontaneously decomposes at ordinary temperatures with production of a green coloration accompanied by development of great heat and emission of a hissing sound; carbonic oxide is eliminated, and the yellowish residue consists chiefly of hydroxylamine hydrochloride. Chloro-formoxime is very poisonous, and has a pungent odour which strongly resembles that of hydrogen cyanide when the vapour is diluted with air; this observation explains the erroneous conclusion that hydrogen



cyanide is formed when fulminic salts are decomposed by hydrochloric acid. Inhaled in small quantities, it induces salivation, laryngital irritation and violent headache, whilst the eyes become painfully inflamed a few hours after exposure to the vapour. The substance is not attacked by water and alcohol; with silver nitrate, it yields silver fulminate, which may be removed in the form of its double salt,  $C:NOAg, C:NOK$ , by extraction with potassium chloride. When silver fulminate is treated with dilute hydrochloric acid at  $0^{\circ}$  (1 mol.), a mixture of chloro-formoxime and its *silver* salt,



is produced (compare Ehrenberg, Abstr., 1885, 38). The latter remains in aqueous solution after extraction with ether, and the addition of hydrochloric acid precipitates silver chloride, which is mixed with silver fulminate if nitric acid is used. This case of a silver salt retaining the metal unattacked in contact with hydrochloric acid is comparable with the behaviour of ethylic sodacetoacetate in the presence of alkyl halogen compounds.

Hydrogen sulphide effects an analogous decomposition of silver fulminate with formation of *silver thioformohydroxamate*,



with silver nitrate, the aqueous solution of this yields silver sulphide and fulminate, and silver sulphide and chloride with hydrochloric acid.

*Phenylisuretine*,  $NPh:CH \cdot NH \cdot OH$ , is formed when chloro-formoxime in ethereal solution is mixed with aniline. It was identified by comparing it with the product obtained from isuretine and aniline hydrochloride. Melting at  $138^{\circ}$ , it dissociates into phenylic isocyanide and hydroxylamine, a decomposition which is also effected by dilute caustic soda.

*Cyanisonitrosoacetohydroxamic acid*,  $HON:C(CN) \cdot C(OH):NOH$ , is obtained by agitating an ethereal solution of chloro-formoxime with small quantities of ammonia until the odour of the latter remains. The acid, formed by decomposing the ammonium salt with dilute hydrochloric acid, crystallises from ether in colourless cubes, which melt and decompose at  $117-118^{\circ}$ . The *monosilver* salt,  $C_3H_2N_3O_3Ag$ , forms flat, yellow prisms, and the *dipotassium* salt,  $C_3HN_3O_3K_2 + H_2O$ , was obtained as a crystalline powder. The action of excess of ammonia on cyanisonitrosoacetohydroxamic acid gives rise to the three substances  $C_3H_4N_4O_2$ ,  $C_3H_5N_3O_3$ , and a syrup yielding the crystalline ammonium salt of the formula  $C_3H_7N_5O_3$ , all isolated by Ehrenberg from chloro-formoxime by treatment with aqueous ammonia (*loc. cit.*); the two latter substances are also obtained by heating the aqueous solution of the acid for two hours on the water-bath.

Caustic potash eliminates ammonia from cyanisonitrosoacetohydroxamic acid, the potassium salt  $C_3HN_2O_4K, H_2O$  being formed, whilst hydrochloric acid decomposes it into oxalic acid, carbonic anhydride, ammonium chloride, and hydroxylamine hydrochloride.

When ethylic cyanisonitrosoacetate is heated with alcoholic ammonia at  $100^{\circ}$ , deoxyfulminuric acid is formed (compare Seidel,

Abstr., 1892, 1117), and since cyanisonitrosoacetic acid is produced by hydrolysis of deoxyfulminuric acid, the latter must be identical with cyanisonitrosoacetamide.

*Sodium ferrofulminate*,  $\text{Na}_4\text{Fe}(\text{ON}\cdot\text{C})_6 + 18\text{H}_2\text{O}$ , is obtained by adding a solution of ferrous sulphate to sodium fulminate (6 mols.) containing a small quantity of caustic soda. On evaporating the liquid, yellow needles a centimetre long are deposited. The aqueous solution is unstable unless caustic soda is present, the liquid rapidly becoming purple; ferric chloride produces an intense purple-red coloration. Removal of the water of crystallisation from this salt involves its dissociation into sodium and ferric fulminates, whilst hydrochloric acid gives rise to chloro-formoxime. Ferric hydroxide and sulphide are produced by the action of caustic soda and ammonium sulphide respectively, and lead acetate, silver nitrate, and mercuric chloride precipitate the corresponding fulminates.

The chief products of the action of ethylic iodide on silver fulminate are ethylic cyanate and cyanurate; at the same time, the author regards the formation of ethylic carboxime  $\text{C}\cdot\text{NOEt}$ , as probable.

*Ethoxyformamidine*,  $\text{NH}_2\cdot\text{CH}\cdot\text{NOEt}$ , is obtained by the action of sodium ethoxide and ethylic iodide on isuretine. It forms a colourless oil which boils at  $170-175^\circ$ , and dissolves readily in water. The *platinochloride* crystallises in yellow quadratic plates, and melts at  $153^\circ$ . Nitrous acid converts ethoxyformamidine into an oil which is probably the ethylic derivative of chloro-formoxime.

M. O. F.

**Carbonyl Nitride and Dicarbamide.** By T. CURTIUS and K. HEIDENREICH (*Ber.*, 1894, **27**, 2684—2685).—*Carbonyl nitride*,  $\text{CO}(\text{N}_3)_2$ , is formed by the action of sodium nitrite on the hydrochloride of carbonylhydrazide,  $\text{CO}(\text{NH}\cdot\text{NH}_2\cdot\text{HCl})_2$ . It is an explosive oil, and when boiled with alcoholic aniline yields carbanilide and diazoimide,  $\text{N}_3\text{H}$ .

*Dicarbamide (bishydrazidicarbonyl)*,  $\text{CO}\langle\begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix}\rangle\text{CO}$ , is obtained by heating ethylic hydrazinedicarboxylate,  $\text{N}_2\text{H}_2(\text{COOEt})_2$ , with hydrazine hydrate at  $100^\circ$ . It crystallises in monoclinic prisms, melts at  $270^\circ$ , and behaves like a monobasic acid; the *ammonium* and *barium* salts crystallise respectively with 1 and 3  $\text{H}_2\text{O}$ ; it, however, also yields a *diammonium* salt. It yields a *benzylidene* derivative,  $\text{C}_2\text{H}_5\text{N}_4\text{O}_2\cdot\text{CHPh}$ , melting at  $253^\circ$ , and it is hydrolysed by strong hydrochloric acid at  $150^\circ$ , yielding carbonic anhydride and hydrazine.

*Methenylcarbohydrazide*,  $\text{CO}\langle\begin{smallmatrix} \text{NH}-\text{N} \\ \text{NH}\cdot\text{NH} \end{smallmatrix}\rangle\text{CH}$ , is formed when ethylic orthoformate is heated with carbohydrazide at  $100^\circ$ . It melts at  $181^\circ$ , behaves like a feeble monobasic acid, and is hydrolysed by hydrochloric acid to carbohydrazide and formic acid. C. F. B.

**Carbamide Derivatives of Tribromopyruvic acid.** By C. BOETTINGER (*Arch. Pharm.*, 1894, **232**, 346—349).—Tribromopyruvic acid decomposes when boiled in aqueous solution; by the action of ammonia at the ordinary temperature, it is converted into oxalic acid,

bromoform, and a little carbonic anhydride, but only two-thirds of the oxalic acid indicated by the equation  $\text{CBr}_3 \cdot \text{C}(\text{OH})_2 \cdot \text{COOH} = \text{CHBr}_3 + \text{C}_2\text{H}_2\text{O}_4$  is produced. When intimately mixed with carbamide or thiocarbamide (2 mol.), it liquefies, and by treatment with alcohol and ether the *carbamide*,  $\text{C}_4\text{H}_7\text{Br}_3\text{N}_2\text{O}_5$ , is obtained; this crystallises in colourless prisms, melts and decomposes at  $125^\circ$ , yields bromoform when boiled with water, and by the action of ammonia is converted into bromoform, oxalic acid, and carbonic anhydride, the last two in molecular proportion. With silver nitrate and mercuric nitrate, white precipitates are formed; the *silver* salt is almost completely soluble in nitric acid; the *mercury* salt is not changed by soda. With concentrated sulphuric acid, the carbamide evolves hydrogen bromide and bromine; the *diureide* is formed along with the carbamide, and may be separated from the latter, as well as from some unaltered acid, by taking advantage of its solubility in ether; it is deposited from water in small, colourless crystals, darkens at  $182^\circ$ , and melts at  $198-199^\circ$ . The *mercuric* salt is colourless, and not altered by soda; the *copper* salt is greenish-blue, and soluble in ammonia; the *silver* salt is colourless, and dissolves in ammonia or nitric acid, but, on heating, silver bromide is precipitated. J. B. T.

**Thiohydantoïnacetic acid and Diphenylthiohydantoïnacetic acid.** By R. TAMBACH (*Annalen*, 1894, 280, 233—246).—*Thiohydantoïnacetic acid*,

$$\begin{array}{c} \text{NH}:\text{C}—\text{S} \\ | \\ \text{NH}:\text{CO} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$$
, is obtained by warming a mixture of thiocarbamide with bromosuccinic acid in molecular proportion. It separates from boiling water in slender, colourless prisms, which decompose without fusion at  $210^\circ$ . The aqueous solution is strongly acid, forming crystalline metallic salts; it also unites with hydrochloric acid. The *ammonium* salt forms colourless, hexagonal prisms, which contain  $1\text{H}_2\text{O}$  and dissociate at  $150^\circ$ . The crystalline form is asymmetric, and the axial ratio  $a : b : c = 0.8833 : 1 : 0.6359$ . The *sodium* salt contains  $3\text{H}_2\text{O}$ , and the *lead* salt is anhydrous. The *hydrochloride* forms large needles which are decomposed by water; the *platinochloride* crystallises with  $1\text{H}_2\text{O}$ .

*Diphenylthiohydantoïnacetic acid*, 
$$\begin{array}{c} \text{NPh}:\text{C}—\text{S} \\ | \\ \text{NPh}:\text{CO} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$$
, is

prepared by boiling together alcoholic solutions of diphenylthiocarbamide and bromosuccinic acid, or by fusing a mixture of these substances in molecular proportion. When recrystallised from alcohol, it melts at  $189-189.5^\circ$ . Desulphurising agents are without action on this and the foregoing acids. The *ammonium* salt dissociates when dissolved in water, and the *hydrochloride*, which melts at  $193-195^\circ$ , exhibits the same property.

*Dioxythiazoleacetic acid*,  $\text{C}_5\text{H}_5\text{O}_4\text{NS}$ , is obtained from thiohydantoïnacetic acid by the action of boiling dilute hydrochloric acid. It forms monosymmetric prisms having the axial ratio  $a : b : c = 2.3449 : 1 : 0.8936$ . It melts at  $168.5-169^\circ$ .

*Phenyldioxythiazoleacetic acid*,  $\text{C}_{11}\text{H}_9\text{O}_4\text{NS}$ , is prepared by boiling diphenylthiohydantoïnacetic acid with dilute hydrochloric acid,

aniline being eliminated; it melts at 146—147°. The *silver* salt is decomposed by light and heat.

When thiohydantoinacetic acid is hydrolysed by means of barium hydroxide, cyanamide and thiomalic acid are formed, whilst diphenylthiohydantoinacetic acid, on similar treatment, gives rise to cyanamide and diphenylthiocarbamide. A characteristic reaction of thiomalic acid is the development of a deep blue coloration on the addition of dilute ferric chloride solution. M. O. F.

**Condensation of Formaldehyde with Alcohols of the Fatty Series in presence of Hydrochloric acid.** By C. FAYRE (*Compt. rend.*, 1894, **119**, 284—286).—A 40 per cent. commercial solution of formaldehyde is mixed with a slight excess of the particular acid, and a current of hydrogen chloride is passed through the mixture, which must be kept cool. After some time, the liquid separates into two layers, the lower of which, more or less strongly coloured, consists of water and the excess of alcohol saturated with hydrochloric acid. The upper layer is purified by fractionation.

The compounds,  $\text{CH}_2\text{Cl}\cdot\text{OR}$ , formed are more stable the higher the molecular weight. They fume in contact with air, and give off an odour of formaldehyde and hydrochloric acid. Water decomposes them, and regenerates formaldehyde, the alcohol, and hydrochloric acid; this action being slower the higher the molecular weight.

Wurtz and Frapoli obtained acetal by means of the reaction  $\text{CH}_3\cdot\text{CHCl}\cdot\text{OEt} + \text{EtONa} = \text{NaCl} + \text{CH}_3\cdot\text{CH}(\text{OEt})_2$ , but the author finds that the same action takes place with the alcohol itself, and in this way he has prepared a series of mixed acetals  $\text{RO}\cdot\text{CH}_2\cdot\text{OR}'$ , which are under investigation.

In order to obtain the formals, the monochlorinated derivatives are heated with a slight excess of the alcohols, and then washed with concentrated sodium hydroxide solution to remove hydrochloric acid. The yield is higher, the higher the molecular weight. The same compounds have been obtained by Trillat and Cambier by a different method: their properties are summarised in the following table.

	Boiling point.	Sp. gr. 15°/4°.	Refractive index, $n_{19}$ .
Chloromethyl ether, $\text{CH}_2\text{Cl}\cdot\text{OMe}$ .....	59° 5'	1·1508	1·389
Dimethylformal, $\text{CH}_2(\text{OMe})_2$ .....	45° 5'	0·872	1·356
Chloromethylic ethylic oxide, $\text{CH}_2\text{Cl}\cdot\text{OEt}$ ..	80° 0'	1·023	1·401
Diethylformal, $\text{CH}_2(\text{OEt})_2$ .....	74° 0'	0·831	1·369
Chloromethylic propylic oxide, $\text{CH}_2\text{Cl}\cdot\text{OPr}$ ..	112° 5'	0·985	1·409
Dipropylformal, $\text{CH}_2(\text{OPr})_2$ .....	140° 5'	0·827	1·391
Chloromethylic isobutylic oxide, $\text{CH}_2\text{Cl}\cdot\text{OBu}$ ..	131° 0'	0·947	1·410
Diisobutylformal, $\text{CH}_2(\text{OBu})_2$ .....	164° 5'	0·837	1·400
Chloromethylic amyllic oxide, $\text{CH}_2\text{Cl}\cdot\text{OC}_5\text{H}_{11}$ ..	154° 0'	1·066	1·425
Diamylformal, $\text{CH}_2(\text{OC}_5\text{H}_{11})_2$ .....	207° 5'	0·841	1·412

**Contraction of Aqueous Solutions of Acetone.** By K. T. P. McELROY (*J. Amer. Chem. Soc.*, 1894, **16**, 618—620).—The acetone used in the experiments was bought as pure, and was further purified by boiling for three days over calcium chloride, and redistilling. The fraction finally used boiled at 56.4°. The method employed was to weigh a flask, add water, weigh, add acetone, re-weigh, shake and determine the specific gravity, first at 20°, and then, without refilling the bottle, at 25°. The weight of the mixture, divided by its specific gravity, gave the actual volume of the mixture at that temperature. The difference between this figure and that representing the sum of the volumes of the unmixed liquids, when divided by the latter figure, gave the percentage of contraction.

The results are tabulated. The contractions, which do not materially vary from each other at 20° or 25°, gradually increase with the amount of water until this reaches 49.9 per cent. After this there is a steady decrease. The highest and lowest percentages of contraction are, respectively, 4.089 (with 49.9 per cent. of water) and 0.861 (with 4.99 per cent. of water).

L. DE K.

**Methyl Octyl Diketone.** By M. FILETI and G. PONZIO (*J. pr. Chem.*, 1894, [2], **50**, 370—378).—When methyl nonyl ketone is treated with nitric acid, it is converted into dinitrononane, methyl octyl diketone, and nonylic acid. Methyl octyl diketone may be isolated from this mixture in the form of the dioxime, from which the free ketone has not yet been obtained in the pure state. It is a yellow liquid, boiling at about 120° under a pressure of 17 mm., and forms a yellow vapour. The *dioxime*,  $\text{NOH}:\text{CMe}:\text{C}(\text{NOH})[\text{CH}_2]_6\text{CH}_2\text{Me}$ , crystallises from dilute alcohol in lustrous plates, melting at 162°. When boiled with dilute sulphuric acid, it yields the *monoxime*, which may also be prepared from methyl nonyl ketone by the action of hydrochloric acid and amylic nitrite. This melts at 56° when prepared from methyl nonyl ketone; at 58° when obtained from the dioxime, and crystallises in nacreous plates, or sometimes in vitreous needles. In spite of the difference in melting point, the authors consider that the two products are identical. *Methyl octyl diketonehydrazoxime*,  $\text{N}_2\text{HPh}:\text{CMe}:\text{C}(\text{NOH})\cdot\text{C}_8\text{H}_{17}$ , forms small, pale yellow prisms, melting at 91—92°. The *hydrazone* crystallises in flat, yellow needles, melts at 91—92°, and is much more stable than the hydrazoxime.

The constitution of the substance as a diketone and not as a keto-aldehyde follows from the decomposition which the monoxime undergoes when it is boiled with dilute sulphuric acid, acetic and nonylic acids being produced along with ammonia.

A. H.

**Chromium Formate.** By C. HAEUSSERMANN (*J. pr. Chem.*, 1894, [2], **50**, 383—384).—This salt is formed when hydrated chromium oxide is dissolved in formic acid (sp. gr. 1.15—1.2), and crystallises in dull dark green matted needles. The air-dried salt has the composition  $\text{Cr}(\text{CHO}_2)_3, 2[\text{Cr}(\text{CHO}_2)_2\cdot\text{OH}] + 4\frac{1}{2}\text{H}_2\text{O}$ , loses water when preserved over sulphuric acid, and, when heated at 100—110°, has the composition  $\text{Cr}(\text{CHO}_2)_3, [\text{Cr}(\text{CHO}_2)_2\cdot\text{OH}] + 1\frac{1}{2}\text{H}_2\text{O}$ .

A. H.

**$\alpha$ -Bromopropionic acid.** By M. WEINIG (*Annalen*, 1894, **280**, 247—252).—The salts of  $\alpha$ -bromopropionic acid are more easily decomposed by water than those of bromacetic acid. The *magnesium* salt contains  $1\text{H}_2\text{O}$ , the *calcium* salt crystallising with  $2\text{H}_2\text{O}$ ; the *lead* and *copper* salts are anhydrous. The *methylic* salt boils at  $140\text{--}150^\circ$ , and its sp. gr. is  $1.499$  at  $21^\circ/4^\circ$ ; the *ethylic* salt boils at  $159.4\text{--}160.2^\circ$ , and has a sp. gr. =  $1.4412$  at  $21.5^\circ/4^\circ$ ; the *isoamyllic* salt boils at  $210\text{--}220^\circ$ . M. O. F.

**$\alpha\beta$ -Dibromisovaleric acid.** By M. ARIFF (*Annalen*, 1894, **280**, 259—262).— $\alpha\beta$ -Dibromisovaleric acid melts at  $107.5\text{--}108^\circ$ ; its salts are very unstable. When the aqueous solution of the sodium salt is boiled, bromobutylene,  $\text{CMe}_2\text{CHBr}$ , is formed; this is a colourless oil which boils at  $91^\circ$ , and is identical with Butlerow's bromisobutylene.

*Bromobutylene dibromide*,  $\text{CBrMe}_2\text{CHBr}_2$ , is obtained by the addition of bromine to the foregoing substance. It boils at  $205\text{--}206^\circ$ , and has sp. gr. =  $2.0169$  at  $20^\circ/4^\circ$ . M. O. F.

**Constitution of Oxybehenic acid.** By M. FILETI and G. BALDRACCO (*J. pr. Chem.*, 1894, [2], **50**, 378—379; compare Abstr., 1894, i, 13).—When monochlorerucic acid is treated with concentrated sulphuric acid, an oxybehenic acid is obtained which is identical with that prepared by a similar process from chlorobrassicic acid. It follows from this that oxybehenic acid is a ketonic acid, and does not possess the structure of an anhydro-acid, in which case the two methods of preparation would have yielded different products. A. H.

**Action of Hydrocyanic acid on Unsaturated Aldehydes.** By G. JOHANNY (*Monatsh.*, 1894, **15**, 415—427; compare Abstr., 1891, 37; Lobry de Bruyn, Abstr., 1885, 242; 1886, 224).—On heating  $\alpha$ -hydroxy- $\beta$ -propylidenebutylamide with baryta, the barium salt of  $\alpha$ -hydroxypropylidenebutylric acid,  $(\text{C}_7\text{H}_{11}\text{O}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ , is obtained. It dissolves readily in water, from which it crystallises in rhombic prisms,  $a : b : c = 1.0296 : 0.9369 : 1$ . It is almost insoluble in alcohol, and, on treatment with an equivalent quantity of sulphuric acid, gives  $\alpha$ -hydroxy- $\beta$ -propylidenebutylric acid; this crystallises in deliquescent white scales and melts at  $43^\circ$ . The acid in chloroform solution gradually absorbs bromine, and is converted into the *dibromide*,  $\text{C}_7\text{H}_{11}\text{O}_3\text{Br}_2$ , which crystallises in triclinic prisms,  $a : b : c = 1.2923 : 1.7737 : 1$ , melts at  $124\text{--}125^\circ$ , and on treatment with dilute alkali forms methylethylacetaldehyde, sodium formate, and the bromolactone,  $\text{C}_7\text{H}_{11}\text{O}_3\text{Br}$ ; the latter crystallises in monoclinic plates  $a : b : c = 0.7938 : 0.6788 : 1$ , and melts at  $82\text{--}83^\circ$ . On reduction with hydriodic acid,  $\alpha$ -hydroxy- $\beta$ -propylidenebutylric acid is first converted into the hexylic iodide,  $\text{CH}_2\text{Et}\cdot\text{CMe}_2\text{I}$ , and finally forms the hexane,  $\text{CH}_2\text{Et}\cdot\text{CHMe}_2$  (compare Wurtz, *Jahresb.*, 1855, 574). G. T. M.

**Unsaturated acids.** By R. FITTIG (*Ber.*, 1894, **27**, 2658—2683).—A lecture delivered before the German Chemical Society, giving a chronological survey of the conclusions arrived at in this field.

M. O. F.

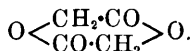
**Dimethylacrylic acid.** By M. WEINIG (*Annalen*, **280**, 252—258).—Diethylaniline is a satisfactory agent for the elimination of hydrogen bromide from such substances as undergo further change by the action of aniline. Dimethylacrylic acid may be prepared in large quantities by boiling together ethylic  $\alpha$ -bromisovalerate with diethylaniline for 5—6 hours in a reflux apparatus; the ethylic salt, which boils at 151°, is then hydrolysed by means of alcoholic potash. The cadmium salt melts and decomposes at 165°; it crystallises with 2H<sub>2</sub>O. The anhydrous copper salt is green. M. O. F.

**Ethylenic Salts of Glycollic and Oxalic acids; Anhydrides of  $\alpha$ -Halogen Fatty Acids.** By C. A. BISCHOFF and P. WALDEN (*Ber.*, 1894, **27**, 2939—2952).—The following ethylenic salts were prepared in order to study their analogy to certain piperazine derivatives from which they differ by the substitution of oxygen for the group NPh (*Abstr.*, 1893, i, 54). The ethylenic salt of glycollic acid,

$O\langle\begin{smallmatrix} CH_2CH_2 \\ CH_2CO \end{smallmatrix}\rangle O$ , may be prepared by acting on monosodioglycol with ethylic chloracetate suspended in benzene. It crystallises in prisms, or long, thin needles, melts at 31°, and boils at 214° under a pressure of 750 mm. Ethylenic oxalate,  $O\langle\begin{smallmatrix} CH_2CH_2 \\ COCO \end{smallmatrix}\rangle O$ , is obtained by distilling a mixture of monethylic oxalate with glycol under a pressure of 5 mm. It forms white crystalline granules, melts at 142—143°, and boils at 196—198° under a pressure of 5 mm. When heated under the atmospheric pressure, carbonic oxide and carbonic anhydride are evolved.

The anhydrides of the  $\alpha$ -halogen fatty acids are best prepared by distilling the acid with phosphoric anhydride.

*Chloracetic anhydride*, (C<sub>2</sub>H<sub>3</sub>ClO)<sub>2</sub>O, boils at 109—111° under a pressure of 10 mm., and solidifies in colourless prisms, melting at 46°. Water gradually converts it into the acid. When treated with potassium carbonate, it is converted into the polyglycollide,



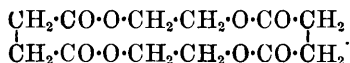
*$\alpha$ -Bromopropionic anhydride* boils at 120° (5 mm.), and when treated with potassium carbonate yields the lactide,  $O\langle\begin{smallmatrix} CHMeCO \\ COCHMe \end{smallmatrix}\rangle O$ , which melts at 124—125°.

*$\alpha$ -Bromobutyric anhydride* boils at 148—152° (10 mm.), and when treated with potassium carbonate yields the inner anhydride of  $\alpha$ -hydroxybutyric acid,  $CHEt\langle\begin{smallmatrix} CO\cdot O \\ O\cdot CO \end{smallmatrix}\rangle CHEt$ .  *$\alpha$ -Bromisobutyric anhydride* boils at 135—140° (35 mm.), melts at 63—65°, and crystallises in plates. Its behaviour towards potassium carbonate is abnormal, methacrylic acid being formed (compare *Abstr.*, 1894, i, 496). A. H.

**Ethylenic Salts of Bibasic Acids and Phenols.** By D. VORLÄNDER (*Annalen*, 1894, **280**, 167—206).—The author's experiments

point to the probable existence of a connection between the nature of an ethylenic salt and the structure of the acid from which it is derived.

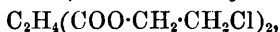
Thus, whilst ethylenic carbonate has the constitution  $\text{CO} < \begin{smallmatrix} \text{O} \cdot \text{CH}_2, \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix}$ , ethylenic succinate is best represented by the formula



This is indicated by a determination of the molecular weight, and by its formation from silver succinate and bischloroethylic succinate.

Ethylenic succinate prepared by heating succinic acid with glycol is identical with the product obtained from silver succinate and ethylenic bromide, or from succinic chloride and disodioglycol. It is readily soluble in chloroform, phenol, and hot nitrobenzene, less freely in acetone, benzene, and boiling alcohol; it separates from the last-named solvent in small, colourless crystals, which melt at 88—90°; when resolidified, it has a sp. gr. = 1.345 at 17°. It is not attacked by benzoic chloride, acetic anhydride, or the alkali carbonates, but hydrolysis is induced by hot caustic alkalis, the corresponding succinate being formed; ethylenic bromide and succinic acid result from the action of hydrobromic acid at 100°. Ammonia gives rise to succinamide, and with phenylhydrazine, succinylphenylhydrazide is obtained. Sodium ethoxide converts the ethylenic salt into ethylic succinosuccinate.

*Ethylic chloroethylic succinate*,  $\text{COOEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Cl}$ , is obtained by the action of succinic chloride on glycol at 70—80°; it boils at 170—172° (30 mm.). *Bischloroethylic succinate*,



which is formed at the same time, boils at 204—205° (30 mm.). It is also produced when succinic chloride acts on ethylene chlorhydrin.

*Ethylichydroxyethylicsuccinate*,  $\text{COOEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , is obtained on heating ethylic succinate with glycol for 15 hours; it boils at 182—183° (25 mm.).

*Ethylenic fumarate*,  $(\text{C}_6\text{H}_6\text{O}_4)_2$ , is obtained by heating silver fumarate with ethylenic bromide for many hours. It melts at 109—110°, and when heated at 150—160° for five hours is converted into a transparent, insoluble, glass-like substance. Ethylenic fumarate is hydrolysed by caustic soda and barium hydroxide, whilst aqueous ammonia converts it into fumaramide. *Ethylenic dibromosuccinate*,  $(\text{C}_6\text{H}_6\text{O}_4\text{Br}_2)_2$ , is formed by the addition of bromine to ethylenic fumarate; it melts at 96°.

*Bischloroethylic fumarate*,  $\text{C}_8\text{H}_{10}\text{O}_4\text{Cl}_2$ , is obtained by warming a mixture of fumaric chloride and ethylene chlorhydrin. It crystallises in lustrous plates which melt at 71°. Conversion into ethylenic fumarate takes place on treating it with silver fumarate.

*Ethylenic maleinate* corresponds in preparation and properties to the fumarate. It cannot be crystallised, and when treated with bromine in ethylenic bromide solution, it yields *ethylenic isodibromosuccinate*, which melts about 80°. *Ethylenic diphenylmaleinate* melts at 112°; it has the formula  $\text{C}_{15}\text{H}_{14}\text{O}_4$ .



When the solution of ethylenic maleinate in chloroform or glacial acetic acid is heated at  $170^{\circ}$  for 4—5 hours, it undergoes molecular rearrangement with formation of the *isomeride*  $(C_6H_6O_4)_2$ , which melts at  $90$ — $92^{\circ}$ ; ethylenic fumarate does not undergo this change. The maleinate, when hydrolysed with barium hydroxide, yields barium fumarate. The *dibromo-additive* compound melts at  $80$ — $82^{\circ}$ . When sodium amalgam is added to a solution of ethylenic fumarate or maleinate in glacial acetic acid, reduction takes place, and ethylenic succinate is formed; this is also obtained by the interaction of bischloroethylic succinate and silver succinate.

Bromacetic bromide acts on glycol at  $50$ — $60^{\circ}$  with formation of  $\beta$ -bromethylic bromacetate,  $CH_2Br \cdot COO \cdot CH_2 \cdot CH_2Br$ , which boils at  $147$ — $148^{\circ}$  (30 mm.); ethylenic bisbromacetate,  $(CH_2Br \cdot COO)_2C_2H_4$ , is produced at the same time; it boils at  $205$ — $206^{\circ}$  (30 mm.).

Ethylenebisquinol,  $C_2H_4(O \cdot C_6H_4 \cdot OH)_2$ , is obtained on heating a mixture of quinol and ethylenic bromide with sodium dissolved in absolute alcohol, in closed vessels at  $95$ — $100^{\circ}$  for five hours; the alkaline mixture is acidified with acetic acid, and the crystalline solid thus obtained is extracted with dilute caustic soda. On adding an acid to this solution, the compound is thrown down, and may be recrystallised from dilute alcohol; it melts at  $219$ — $220^{\circ}$ , and reduces Fehling's solution when boiled with it. The *diacetyl* derivative melts at  $137$ — $138^{\circ}$ ; the *diethylic* salt at  $149^{\circ}$ . Interaction with bromacetic bromide gives rise to the *bisbromacetyl* derivative,  $C_{18}H_{16}O_6Br_2$ , which forms long, lustrous plates, and melts at  $156^{\circ}$ . The portion of the crude preparation of ethylenebisquinol, which is insoluble in caustic soda, melts at  $238^{\circ}$ .

Ethylenecatechol,  $C_6H_4 < \begin{smallmatrix} O \cdot CH_2 \\ O \cdot CH_2 \end{smallmatrix}$ , is prepared similarly to the foregoing compound; it is a colourless oil which boils at  $124^{\circ}$  (25 mm.), and distils under ordinary pressure at  $216^{\circ}$ . The *mononitro-derivative* melts at  $121^{\circ}$ .  
M. O. F.

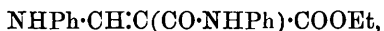
**Chlorinated Succinic acids and Chloromaleic acid.** By B. DE S. J. VAN DER RIET (*Annalen*, 1894, **280**, 216—232).—Isodichlorosuccinic anhydride is obtained by exposing to sunlight a solution of maleic anhydride in liquid chlorine contained in a sealed tube; the corresponding acid melts at  $170^{\circ}$  (compare Michael and Tissot, *Abstr.*, 1893, i, 143). The *dimethylic* and *diethylic* salts of isodichlorosuccinic acid are colourless oils, from which hydrogen chloride is eliminated spontaneously or by the application of heat. The *ammonium* salt contains  $2H_2O$ , the *calcium* and *copper* salts crystallise with  $2\frac{1}{2}H_2O$ , and the *lead* salt with  $3H_2O$ ; the *barium* and *strontium* salts contain  $7H_2O$ .

When isodichlorosuccinic anhydride is heated in a reflux apparatus until the evolution of hydrogen chloride ceases, an almost quantitative yield of chloromaleic anhydride is obtained, boiling at  $194^{\circ}$ . Treatment of this substance with water gives rise to the chloromaleic acid obtained from trichloroacetyl- $\beta$ -chloroacrylic acid (compare Zincke, *Abstr.*, 1893, i, 318); the *strontium* salt forms silvery crusts containing  $4\frac{1}{2}H_2O$ .

Elimination of hydrogen chloride from dichlorosuccinic acid by means of hot aqueous sodium acetate yields chloromaleïc acid as the sole product, and the conclusion of Michael and Tissot (*loc. cit.*) that chlorofumaric acid is formed must therefore be attributed to the transformation of chloromaleïc acid into this substance under the influence of caustic alkali, this hydrolytic agent having been employed by the investigators named.

*Trichlorosuccinic acid* is formed when a mixture of 20 grams of chloromaleïc acid with 10 c.c. of water and 30 grams of liquid chlorine is exposed to sunlight for several hours in a sealed tube. The acid forms a colourless, highly-deliquescent crystalline mass, which gives no precipitate with silver nitrate; the metallic salts do not crystallise well. The *aniline* salt,  $(\text{NH}_2\text{Ph})_2\text{C}_4\text{H}_3\text{Cl}_3\text{O}_4$ , melts at  $146^\circ$ ; the *orthotoluidine* salt contains 1 mol. of alcohol, and decomposes before it melts. M. O. F.

**Ethylic Amidoethylenedicarboxylate.** By S. RUHEMANN and R. S. MORRELL (*Ber.*, 1894, **27**, 2743—2747).—Ethylic dicarboxyglutaconate reacts with aniline in the same way as with ammonia, *ethylic anilidoethylenedicarboxylate*,  $\text{NHPh}\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$ , being obtained together with ethylic malonate. The anilido-compound forms colourless crystals melting at  $48\text{--}49^\circ$ . Ethylic amidoethylenedicarboxylate is converted by ammonia into a monamide (*Trans.*, 1892, 791), and reacts in a similar manner with aniline, ammonia being evolved and the *monanilide* of *ethylic anilidoethylenedicarboxylate*,



formed; this substance crystallises in yellowish needles, and melts at  $118^\circ$ . A small amount of the monanilide is further decomposed, malondianilide and diphenylformamidine being produced. Similar results have been independently obtained by Band (*Inaug. Dissert.*, Leipzig, 1894).

Ethylic amidoethylenedicarboxylate is converted by hydrazine into ethylic isopyrazolonecarboxylate,  $\text{COOEt}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , whilst with phenylhydrazine, it yields ethylic phenylisopyrazolonecarboxylate.

A. H.

**Disubstituted Succinic acids.** By H. KIRCHHOFF (*Annalen*, 1894, **280**, 207—215).—Maleïc anhydride unites with bromine at ordinary temperatures, isodibromosuccinic acid being formed; the *calcium* salt has the constitution  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4\text{Ca} + 3\text{H}_2\text{O}$ . Dichlorosuccinic acid is prepared by exposing to sunlight fumaric acid in contact with liquid chlorine contained in a sealed tube (compare Michael and Tissot, *Abstr.*, 1893, i, 142). The *silver* and *barium* salts are anhydrous, the *strontium* salt crystallises with  $1\text{H}_2\text{O}$ , the *calcium* salt with  $2\text{H}_2\text{O}$ , the *zinc*, *copper*, and *cadmium* salts with  $3\text{H}_2\text{O}$ . The *dimethylic* and *diethylic* salts melt respectively at  $31\cdot5\text{--}32^\circ$  and  $62^\circ$ .

M. O. F.

**Synthetical Formation of Mesotartaric acid and Racemic acid.** By F. POLLAK (*Monatsh.*, 1894, 15, 469—488).—In 1864, Schöyen prepared an acid by the action of alkalis on the additive product of glyoxal and hydrocyanic acid; he was unable to obtain it in a crystalline form, but, from the properties of its salts, it appeared to be a new isomeride of tartaric acid, and was, therefore, termed glycotartaric acid. Four years later, Strecker examined the products of the action of hydrochloric acid on the same additive compound, and obtained racemic acid, which he found to be quite different from Schöyen's acid. Since this time, no further investigation has been made, and the author has, therefore, taken the matter up again, and has succeeded in isolating the additive product of glyoxal and hydrocyanic acid, and also, to a large extent, in explaining the different results obtained by Schöyen and Strecker.

To prepare the cyanhydrin from glyoxal, it is necessary to avoid the presence of water, as decomposition then readily takes place: the most favourable results are obtained by heating an alcoholic solution of glyoxal with a 5 per cent. excess of alcoholic hydrogen cyanide at 80—90°, distilling off the alcohol in a vacuum, and allowing the syrupy residue to remain for some hours, when it solidifies to a magma of crystals. This, when treated with absolute ether, leaves a brownish, resinous mass, from which no definite substance could be obtained; the filtrate, on evaporation, yields a crystalline substance, which, after separating from the syrupy mother liquor and recrystallising, forms monosymmetric tablets,  $a : b : c = 0.8627 : 1 : 1.4782$ ,  $e = 90^\circ 49.5'$ , and melts and is entirely decomposed at 131°; the analysis and molecular weight determination agree with the constitutional formula  $\text{CN} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ . With benzoic chloride and alkali, it yields a *dibenzoyl* derivative melting at 67—69°, and, on heating with acetic anhydride at 60°, it is converted into the *diacetyl* derivative,  $\text{CN} \cdot \text{CH}(\text{OAc}) \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$ , which crystallises in lustrous, rhombic tablets,  $a : b : c = 0.7150 : 1 : 0.6809$ , melts at 75—77° (corr.), is readily soluble in the common solvents, and is optically inactive.

When treated with hydrochloric acid, it is converted into mesotartaric acid, which was identified by its physical properties and those of its calcium salt; the yield is very good, and no trace of any isomeride could be detected in the products of the action. The nitrile must, therefore, be regarded as *mesotartaric nitrile*. Strecker's inability to find this acid among the products of the action of hydrochloric acid on the crude nitrile is probably due to the fact that he extracted his calcium salts with an acetic acid solution, in which freshly prepared calcium mesotartrate is soluble.

The mother liquor from the mesotartaric nitrile does not deposit any more crystals, even after many weeks, but if it is heated with acetic anhydride at 60°, the product dissolved in ether, filtered, and the solution evaporated, a syrupy residue is left which after a time deposits crystals; by fractional crystallisation from ether, these may be separated into two crystalline compounds, one of which is diacetylmesotartaric nitrile, and the other an isomeric acetyl derivative, which crystallises in monosymmetric plates or prisms,  $a : b : c =$

1.2569 : 1 : 2.6102,  $\alpha_c = 97^\circ 15'$ , and melts at  $97-98^\circ$  (corr.). It is converted by the action of hydrochloric acid into racemic acid, and must, therefore, be *diacetylracemic nitrile*. The racemic acid thus prepared agrees in all its properties with the natural acid.

It appears probable that the racemic nitrile is not formed by the direct action of hydrogen cyanide on glyoxal, as the mother liquor from the mesotartaric nitrile does not yield it, if it is worked up at once, and the racemic derivative is therefore probably formed from the impure mesotartaric nitrile on long-continued standing. It is not formed by the action of acetic anhydride, as all attempts to bring about the change of the diacetylmесotartaric nitrile into the isomeride under similar conditions were without success.

Schöyen's glycotartaric acid was, in all probability, a mixture of mesotartaric acid with glycollic acid, the latter being formed by the action of alkalis on unaltered glyoxal still present. H. G. C.

**Synthesis of Comenic acid: Chloropyromeconic acid.** By A. PERATONER and R. LEONE (*Gazzetta*, 1894, **24**, ii, 75—85).—Pyromeconic acid is readily prepared by subliming meconic acid at  $260-310^\circ$  in a current of carbonic anhydride, and treating the product with chloroform, in which it is very soluble; the comenic and meconic acids remain undissolved. Pyromeconic acid, when purified by resublimation, melts at  $117^\circ$ , but at  $119-120^\circ$  when contaminated with traces of comenic acid. Cryoscopic determinations in acetic acid solution show that pyromeconic acid has a molecular weight corresponding with the formula  $C_8H_4O_3$ .

Pure sodium pyromeconate,  $C_8H_3O_3Na$ , separates on treating a benzene solution of the acid with sodium. On heating it at  $196^\circ$  with carbonic anhydride under pressure, it is partly converted into sodium comenate. Comenic acid is therefore a carboxyl-derivative of pyromeconic acid.

*Monochloropyromeconic acid*,  $C_8H_3ClO_3$ , is obtained on treating pyromeconic acid with sulphuryl chloride; it crystallises in long, colourless, flattened needles, which melt at  $181^\circ$  and sublime at the ordinary temperature. It does not decompose alkali carbonates, and is very soluble in organic solvents or water.

Meconic and comenic acids do not react with sulphuryl chloride.

W. J. P.

**Furfurylic and other Nitrites.** By G. BERTONI (*Gazzetta*, 1894, **24**, ii, 20—25).—*Furfurylic nitrite*,  $C_4OH_3 \cdot CH_2 \cdot ONO$ , may be readily prepared by gradually adding trinitroglycerol to furfurylic alcohol cooled by a freezing mixture. It separates as a heavy, yellowish oil possessing a not unpleasant odour; in a few days it turns brown and resinifies. It is soluble in ether, chloroform, or glycerol, but is insoluble in water; the acetic acid solution soon decomposes. Potash, mineral acids, and methylic or ethylic alcohol immediately decompose the nitrite; hydrogen sulphide and ammonium sulphide act on it with separation of sulphur. Furfurylic nitrite has a sp. gr. of 1.165 at  $11^\circ$ ; it remains unchanged at  $100^\circ$ , but at  $126-127^\circ$  it begins to boil violently and decomposes, leaving an

abundant carbonaceous residue. The following nitrites were prepared by processes similar to the above.

*Isobutyleneglycollic nitrite*,  $\text{NO} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}$ , is very sensitive to light and is decomposed by water or acids. It has a sharp taste, boils and decomposes at  $128^\circ$  with evolution of red vapours, and has a sp. gr. of 1.092 at  $0^\circ$ . Methyllic alcohol reconverts it into the glycol.

*Ethylenic acetone nitrite*,  $\text{CH}_3 \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}$ , gives off nitrous oxide when in contact with water, has a pleasant ethereal odour, and boils at  $130^\circ$ .

*Ethylenechlorhydrin nitrite*,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}$ , has an unpleasant, penetrating odour, and continually evolves chlorine and nitrous oxide; at  $117^\circ$  it boils and decomposes.

*Dichlorhydrin nitrite*,  $\text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}$ , resembles the preceding nitrite, and is converted into the dichlorhydrin by methyllic alcohol; it boils and decomposes at  $155\text{--}160^\circ$ .

*Chloral nitrite*,  $\text{CCl}_3 \cdot \text{CH}(\text{O} \cdot \text{NO})_2$ , is a heavy, unstable oil, which begins to boil at  $70^\circ$ , and is totally decomposed at  $75^\circ$ .

*Cetylic nitrite*,  $\text{C}_{16}\text{H}_{33} \cdot \text{O} \cdot \text{NO}$ , is fairly stable, and melts at about  $20^\circ$ ; it decomposes at  $190\text{--}200^\circ$ , evolving nitric oxide in abundance.

W. J. P.

**$\alpha\alpha$ -Dithienyl.** By O. EBERHARD (*Ber.*, 1894, **27**, 2919).— $\alpha\alpha$ -Dithienyl may be obtained by heating  $\alpha$ -iodothiophen with silver, prepared by means of an alkaline solution of glucose, and is identical with the dithienyl obtained by Töhl. On oxidation with a boiling solution of potassium permanganate, it is converted into  $\alpha$ -thiophenic acid.

Dithienyl is not formed when  $\alpha$ -bromo- or  $\alpha$ -iodo-thiophen is treated with sodium in presence of ether or when the iodo-derivative is heated with zinc-dust or with silver reduced by means of ferrous sulphate.

A. H.

**Preparation of Phenylnitromethane.** By S. GABRIEL (*Ber.*, 1894, **27**, 2738).—In view of the criticism of Werner and Buss (*Ber.*, **27**, 2193), the author has had the method of preparation of phenyl-nitromethane, which has been already described by him (*Ber.*, **18**, 1251), carried out afresh, and finds that it is perfectly satisfactory.

A. H.

**Ethereal Salts of Catechol with Phosphorous and Sulphurous Acids.** By R. ANSCHÜTZ and W. POSTH (*Ber.*, 1894, **27**, 2751—2753).—*Catechol phosphite*,  $\text{P}_2(\text{O}_2 \cdot \text{C}_6\text{H}_4)_3$ , is formed when catechol is heated in benzene solution with phosphorus trichloride. It is a colourless liquid, boils at  $202\text{--}203^\circ$  under a pressure of 1 mm., and, on exposure to air, rapidly changes into a solid substance melting at  $100\text{--}101^\circ$ ; this has not yet been further investigated.

*Catechol sulphite*,  $\text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{SO}$ , is obtained in a similar manner from catechol and thionyl chloride. It is a colourless, mobile liquid, boils at  $210\text{--}211^\circ$ , and has a sp. gr. = 1.409 at  $15^\circ$ . Its vapour has an unpleasant odour, and causes a flow of tears.

A. H.

**Action of Phosphorus Pentachloride on Tetrachloroquinone.**

By E. BARRAL (*Compt. rend.*, 1894, **119**, 280—281).—When quinone (1 mol.) and phosphorus pentachloride (2 mols.) are heated together at 130—140° for many hours, they yield a yellow liquid, which, on cooling, solidifies to a white solid. The action is accelerated by the presence of a small quantity of phosphorus trichloride. The product is thrown into water, washed, dried, and heated with hot benzene, which leaves an abundant residue, probably consisting of pentachlorophenol phosphate. The benzene solution, when very slowly evaporated, yields a mixture of long needles of hexachlorobenzene and large prisms of hexachlorobenzene dichloride, impregnated with oily matter which has the odour of chloroquinone. The hexachlorobenzene dichloride melts at 159—160°, and is identical with that previously described (*Abstr.*, 1894, i, 406). It crystallises from light petroleum in long prisms, and from benzene in large, monoclinic prisms. It sublimes without change at a temperature below 200°, but if more strongly heated decomposes into hexachlorobenzene and chlorine. In presence of phosphorus pentachloride, decomposition takes place at a temperature much below 200°, and this probably explains why Graebe obtained hexachlorobenzene only on heating tetrachloroquinone with phosphorus pentachloride at 180°. Fuming nitric acid oxidises hexachlorobenzene dichloride to tetrachloroquinone. It would follow that quinone is a true diketone. C. H. B.

**Diisosaftrole and Cubebin.** By A. ANGELI and P. MOLE (*Gazzetta*, 1894, **24**, ii, 127—130).—*Diisosaftrole* ( $C_{10}H_{10}O_2$ )<sub>2</sub>, is prepared by heating isosaftrole with a saturated alcoholic solution of hydrogen chloride at 160° in closed tubes. It crystallises in thin, white needles sparingly soluble in cold alcohol; it melts at 145°, and is found, by cryoscopic determinations, to have the molecular composition indicated above.

The authors were unable to prepare Weidel's tribromocubebin (*Jahresb.*, 1877, 931), but obtained *dibromocubebin*,  $C_{10}H_8Br_2O_2$ , by direct bromination of cubebin. The new derivative forms small, white crystals melting at 229°.

Isosaftrole and cubebin are undoubtedly very nearly related, and the authors have undertaken their investigation with the object of throwing some light on the constitution of cubebin. W. J. P.

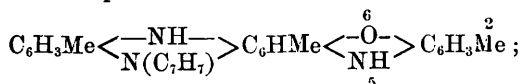
**Sulphur in Aniline and Paramidophenol, and the Calcium Hypochlorite Reaction.**

By A. HANTZSCH and H. FREESE (*Ber.*, 1894, **27**, 2966—2968).—The aniline employed was prepared from benzene which had been purified with sulphuric acid: it was boiled for 10 hours with 10 per cent. of acetone; the quantity of sulphur found varied from 0.0027—0.0041 per cent. Further experiments show that aniline, from the most varied sources and of undoubted purity, gives the calcium hypochlorite reaction (compare *Abstr.*, 1894, i, 572); nitro-, dinitro-, and amido-thiophen do not. So far, the previous conclusions must be amended; but there appears to be a connection between the browning of aniline and the sulphur which it contains. J. B. T.

**Oxidation of Aromatic Orthodiamines and Orthamidophenols.** By O. FISCHER and O. JONAS (*Ber.*, 1894, **27**, 2782—2785).—The oxidation product of orthoamidoditolyamine previously described by Fischer and Sieder (*Abstr.*, 1891, 434), has been again analysed, and its molecular weight determined, it appears to be an

indone,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} 6 \\ \text{<---N} \\ \text{N(C}_7\text{H}_7\text{)} \end{smallmatrix} \begin{smallmatrix} 2 \\ \text{>} \end{smallmatrix} \text{C}_6\text{HMeO} \cdot \text{NHC}_7\text{H}_7$ . The corresponding

induline could not be isolated. By the action of alcoholic potash, the indone is converted into an isomeric compound which is probably a fluorindine- or triphenioxazine-derivative



it crystallises in red needles, melts at  $260^\circ$ , is a strong base, and gives a violet coloration with sulphuric acid.

Orthamidophenol, when oxidised with mercuric oxide, yields the

compound  $\text{C}_6\text{H}_4 \begin{smallmatrix} 2 \\ \text{<N} \\ \text{O} \end{smallmatrix} \begin{smallmatrix} 1,4 \\ \text{>} \end{smallmatrix} \text{C}_6\text{H}_2\text{O} \cdot \text{NH}_2$ , the analogue of diamidophenazine;

this crystallises in small, dark red crystals, melts at  $249^\circ$ , is insoluble in alkalis, and, with sulphuric acid, gives a violet coloration, changing to red on dilution. The *hydrochloride* crystallises in dark brown needles; the *platinochloride* forms deep red, lustrous crystals: both are sparingly soluble; the *aurochloride* crystallises in bronze-coloured, lustrous needles.

It is characteristic of the benzeneorthodiamines and orthamidophenols that on oxidation 2 mols. combine to form phenazine- and phenoxazine-derivatives, whilst the corresponding naphthalene compounds yield quinones; this is probably the reason of the difficulty which is experienced in preparing benzeneorthoquinones by methods similar to those which readily yield 1-2-naphthaquinones.

J. B. T.

**Stereoisomeric Potassium Benzenediazosulphonates.** By E. BAMBERGER (*Ber.*, **27**, 2930—2939; compare *Ber.*, 1894, **27**, 2586).—The author criticises in detail the arguments put forward by Hantzsch (*Abstr.*, 1894, i, 597) in support of his view, that the orange and yellow salts obtained by the action of potassium sulphite on diazobenzene salts are stereoisomeric. The orange salt has all the properties of a sulphite, evolves sulphurous anhydride when treated with dilute acids, decolorises iodine and potassium permanganate solutions, and reduces cupric thiocyanate. Attempts to repeat the analysis of the salt show that trustworthy numbers cannot be obtained owing to the rapid decomposition and molecular change which occur. The author considers that all the properties of the orange salt indicate that it is a complex diazobenzene sulphite, the spontaneous change of which into a sulphonate would be quite in accordance with our knowledge of the relations between the sulphites and sulphonates of the fatty series.

A. H.

**Formation of Dyes from Stereoisomeric Diazo-compounds, and the Configuration of Diazo-ethers.** By A. HANTZSCH (*Ber.*, 1894, **27**, 2968—2975).—A polemical reply to Bamberger's criticisms (*Abstr.*, 1894, i, 580) of the author's recent communications on stereoisomeric diazo-compounds. It is admitted that the author was in error in considering the diazoamido-compounds and bisdiazoamido-compounds as stereoisomeric; the difference in composition is small, and the latter compounds are readily, often spontaneously, converted into the former. Potassium nitroantidiazobenzene reacts in the course of a few seconds with sodium  $\beta$ -naphthol containing a little free alkali; the action is slower the larger the quantity of free alkali present. Potassium benzeneantidiazosulphonate, the yellow stable salt, reacts in a similar manner, but more slowly. Anti(iso)-diazo-derivatives, therefore, as such, combine with alkali phenols, but less rapidly than the syn-derivatives: the difference is merely one of degree, as is usually the case with stereoisomeric compounds. Nitrodiazobenzene methyl ether closely resembles sodium nitrodiazobenzene in its action on naphthol, but with alkali in excess the solution becomes instantaneously violet; this difference is not due to hydrolysis of the ether, but arises from the fact that the alkali, although without direct action on the ether, exerts considerable influence on solutions of the sodium salt or on diazo-derivatives with acidic properties. The violet colour is caused by the formation of a sodium salt which is much more readily soluble than the red dye itself, and is, therefore, more easily formed. The direct proof that the ether is an "anti"-derivative can only be afforded by the preparation of the "syn"-compound; but it is unlikely that this can exist, as, in addition to the characteristic instability of "syn"-derivatives, it would be hydrolysed with the greatest ease. J. B. T.

**Reduction Products of Azo-compounds.** By P. JACOBSON and P. PIEPENBRINK (*Ber.*, 1894, **27**, 2700—2714).—When metatolueneazoparacresetol,  $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot OEt$  [ $N:Me:OEt = 1:3:6$ ], is reduced with stannous chloride and hydrochloric acid, it undergoes the benzidine transformation, yielding a diphenyl-derivative, dimethylethoxydiamidodiphenyl,  $NH_2 \cdot C_6H_3Me \cdot C_6H_2Me(NH_2) \cdot OEt$  [ $Me_2:(NH_2)_2:OEt = 2:2':4:4':5$ ]. But when paratolueneazoparacresetol,  $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot OEt$ , in which the Me of the  $C_6H_4Me$ -group occupies the para-position, is reduced, a benzidine transformation is no longer to be expected, and, in fact, a diphenyl-derivative (boiling at  $237-243^\circ$  under 35 mm. pressure, and yielding a yellow orthohydroxybenzylidene-derivative which melts at  $106^\circ$ ) is only formed in small amount; the main action is a semidine transformation, with formation of a diphenylamine-derivative, dimethylethoxyamidodiphenylamine,

$C_6H_4Me \cdot NH \cdot C_6H_2Me(NH_2) \cdot OEt$  [ $NH:Me:NH_2:OEt = 1:2:4:5$ ]; but at the same time some of the azo-compound is decomposed, with formation of paratoluidine and a cresetidine, [ $NH_2:Me:OEt = 1:3:6$ ].

*Metatolueneazoparacresol*, prepared by diazotising metatoluidine and treating the product with paracresol, is a brown substance melting at  $95^\circ$ . When boiled with sodium ethoxide and ethylic bromide in



alcoholic solution, it yields the *cresetol*, which melts at  $76^{\circ}$ . *Dimethylethoxydiamidodiphenyl* yields a *dihydrochloride* and a yellow *di-orthohydroxybenzylidene*-derivative melting at  $127^{\circ}$ .

Paratolueneazoparacresetol melts at  $43^{\circ}$ ; not at  $171^{\circ}$ , as Noelting and Werner state (Abstr., 1891, 214). *Dimethylethoxyamidodiphenylamine* melts at  $108$ – $109^{\circ}$ ; with acetic acid, it yields a *monacetyl*-derivative melting at  $125^{\circ}$ ; with carbon bisulphide, a *thiocarbamide* melting at  $167.5^{\circ}$ . The *orthohydroxybenzylidene* derivative melts at  $157^{\circ}$ . With acetic chloride, it yields a *diacetyl* derivative melting at  $165^{\circ}$ ; and, when oxidised with chromic acid, a red *ethoxytoluquinonetoluidide*,  $C_6H_4Me:N:C_6H_2MeO:OEt$ , is found melting at  $76^{\circ}$ . The latter yields paratoluidine when hydrolysed; the other product, presumably ethoxytoluquinone, could not be isolated. C. F. B.

**Derivatives of 2:4-Dinitrophenylhydrazine and Picrylhydrazine; Action of Hydrazine Hydrate on Chloranil.** By A. PURGOTTI (*Gazzetta*, 1894, **24**, i, 554–584; compare Abstr., 1894, i, 372, and next abstract).—2:4 Dinitrophenylhydrazine,  $C_6H_3(NO_2)_2NH:NH_2$ , is prepared by boiling an alcoholic solution of 1:2:4-metadinitrochlorobenzene and hydrazine hydrate; it forms transparent yellow crystals having a red fluorescence, or small pleochromatic prisms melting at  $194^{\circ}$ . It dissolves sparingly in the usual solvents, and is decomposed by soda with formation of 1:2:4-metadinitrophenol. The *hydrochloride* crystallises in yellow, pleochromatic needles which lose hydrogen chloride at  $110^{\circ}$ , leaving the base; it melts at  $150^{\circ}$  in a closed tube.

*Acetyl*-2:4-dinitrophenylhydrazine,  $C_6H_3(NO_2)_2N_2H_2Ac$ , obtained by heating the base with acetic acid, crystallises in thin, yellow pleochromatic needles melting at  $193$ – $194^{\circ}$ .

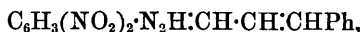
*Oxaldinitrodiphenylhydrazine*,  $C_2O_2[N_2H_2 \cdot C_6H_3(NO_2)_2]_2$ , is prepared by heating a mixture of ethylic oxalate with the dinitrophenylhydrazine. It forms yellow crystals which darken at  $270^{\circ}$ , and melt at  $292^{\circ}$ .

2:4-Dinitrodiphenylthiosemicarbazide,  $NHPh \cdot CS:N_2H_2 \cdot C_6H_3(NO_2)_2$ , prepared by boiling the base with phenylthiocarbimide in alcoholic solution, forms yellow, lustrous, tabular crystals melting at  $186^{\circ}$ ; it is decomposed by soda, and by boiling water. The hydrazine is converted into 2:4-dinitrophenylazoimide,  $\begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > N \cdot C_6H_3(NO_2)_2$ , by dissolving it in sulphuric acid, and treating it with sodium nitrite.

2:4-Dinitrophenylhydrazomethane,  $C_6H_3(NO_2)_2NH:N:CH_2$ , separates on mixing formaldehyde with the hydrazine dissolved in dilute sulphuric acid; it separates from its alcoholic solution in tiny yellow crystals melting at  $155^{\circ}$ . The corresponding *ethane* derivative is obtained from acetaldehyde, and crystallises in yellow scales melting at  $147^{\circ}$ . The *benzylidene* derivative,  $C_6H_3(NO_2)_2NH:N:CHPh$ , prepared from benzaldehyde, crystallises in microscopic yellow needles and melts at  $203^{\circ}$ . The *orthohydroxybenzylidene* derivative,  $C_6H_3(NO_2)_2N_2H:CH \cdot C_6H_4OH$ , prepared from salicylaldehyde, crystallises in minute yellow needles melting at  $237^{\circ}$ ; its *para*-isomeride is amorphous and melts at  $157^{\circ}$ . The *orthonitrobenzylidene* derivative

is obtained from orthonitrobenzaldehyde and melts at about  $192^{\circ}$ ; its *meta*-isomeride melts at  $268^{\circ}$ .

*Cinnamylidene-2 : 4-dinitrophenylhydrazine*,



prepared from cinnamaldehyde, crystallises in small, bright red scales.

*Furfurylidenedinitrophenylhydrazine*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2\text{H} : \text{CH} : \text{C}_4\text{H}_2\text{O}$ , is obtained from furfuraldehyde, and crystallises in scarlet laminæ melting at  $202^{\circ}$ .

*Dinitrophenylhydrazopropane*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2\text{H} : \text{CMe}_2$ , crystallises in minute, yellow tablets melting at  $118^{\circ}$ .

*Ethylidene dinitrophenylhydrazoacetoacetate*,



is obtained by the action of ethylic acetoacetate on the hydrazine; it crystallises in thin, yellow needles melting at  $95^{\circ}$ .

*Dinitrophenylhydrazobenzophenone*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2\text{H} : \text{CPh}_2$ , obtained from benzophenone, forms small, orange-yellow needles melting at  $229^{\circ}$ .

*Dinitrophenylhydrazobenzile*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2\text{H} : \text{CPh} : \text{COPh}$ , is obtained from benzile, and crystallises in very minute orange-yellow laminæ melting at  $183$ — $184^{\circ}$ .

*Acetylpicrylhydrazine*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_2\text{H}_2\text{Ac}$ , is prepared by boiling an acetic acid solution of picrylhydrazine; it crystallises in very thin, yellow needles melting at  $210^{\circ}$ .

*Oxaldipicrylhydrazine*,  $\text{C}_2\text{O}_2[\text{N}_2\text{H}_2 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ , prepared from ethylic oxalate and picrylhydrazine, crystallises in yellowish needles melting at  $175^{\circ}$ .

*Picrylazoimide*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_3$ , crystallises in thin, yellow needles melting at  $70^{\circ}$ .

*Ethylidenepicrylhydrazine*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_2\text{H} : \text{CHMe}$ , is obtained in red laminæ melting at  $119$ — $120^{\circ}$ .

*Benzylidenepicrylhydrazine*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_2\text{H} : \text{CHPh}$ , is obtained in thin, yellow needles melting and decomposing at  $248^{\circ}$ . *Orthonitrobenzylidenepicrylhydrazine* and its *meta*-isomeride form small, yellow crystals melting at  $215^{\circ}$  and  $250$ — $251^{\circ}$  respectively.

*Orthohydroxybenzylidenepicrylhydrazine*,



and its *para*-isomeride are obtained as crystalline powders melting and decomposing at  $275^{\circ}$  and  $284^{\circ}$  respectively.

*Cinnamylidenepicrylhydrazine* is obtained in small, red crystals melting at  $200^{\circ}$ . *Furfurylidenepicrylhydrazine* forms small, yellow crystals having a red fluorescence and melting at  $230^{\circ}$ .

*Picrylhydrazopropane* and the *picrylhydrazone* of ethylic acetoacetate crystallise in yellow needles melting at  $125^{\circ}$  and  $165^{\circ}$  respectively.

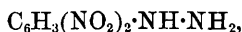
Chloranil dissolves in a warm alcoholic solution of hydrazine hydrate with evolution of nitrogen and formation of a compound of hydrazine and tetrachloroquinol,  $\text{C}_6\text{Cl}_4(\text{OH})_2 \cdot 2\text{N}_2\text{H}_4$ ; it crystallises in small needles melting at  $183^{\circ}$ .

W. J. P.

**Synthesis of Aromatic Hydrazines from Hydrazine Hydrate.**

By T. CURTIUS and G. M. DEDICHEN (*J. pr. Chem.*, 1894, [2], 50, 241—274; compare preceding abstract).—Hydrazine hydrate does not yield aromatic hydrazines when heated, in presence of caustic baryta, with iodobenzene, paranitraniline, paraiodo- or parabromo-nitrobenzene, or the para-halogen substitution derivatives of aniline.

On the other hand, it reacts in the cold with 1 : 2 : 4-chloro- or bromo-dinitrobenzene to form 2 : 4-dinitrophenylhydrazine,



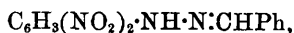
which crystallises from alcohol in splendid, deep violet, flat prisms, melting and decomposing at 198°. It is very sparingly soluble in cold alcohol, insoluble in water and cold acids, readily soluble in alkalis, and reduces Fehling's solution and ammoniacal silver oxide solution. It is very stable towards acids, and may be recrystallised from glacial acetic acid. The *hydrochloride* crystallises in yellow, lustrous plates, which are decomposed by water and alcohol, the free base being formed; the whole of the acid is lost at 150°. The *nitrate* forms small, hard, nacreous plates, and, like the hydrochloride, is decomposed by water and alcohol, but melts at 158—160° without decomposing.

The hydrazine dissolves readily in alkalis, forming deep red solutions, which decompose on boiling, dinitrophenol being formed and ammonia evolved. The *sodium* salt probably has the formula  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NNa} \cdot \text{NH}_2$ , and is an amorphous, reddish-yellow mass, which decomposes very readily and explodes when heated. Dinitrophenylhydrazine does not appear to combine directly with carbon bisulphide. *Acetyldinitrophenylhydrazine*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{NHAc}$ , is obtained by the action of acetic anhydride on the base, and crystallises in slender, pale yellow, silky needles, melting at 197—198°; alkalis give with it a red coloration, which changes to light yellow on the addition of an acid.

*Dinitrophenylnitrosohydrazine*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}(\text{NO}) \cdot \text{NH}_2$ , is obtained as an oil, which solidifies to a crystalline mass; it melts at 72°, and deflagrates when heated in a test-tube. It decomposes when kept, and is also partially decomposed by boiling alcohol, but may be recrystallised from ether, from which it separates in large, thick prisms; these, however, soon fall to a yellow powder.

*Dinitrophenylazoimide*,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_3$ , is formed when the nitroso-compound is boiled with water or allowed to stand in a desiccator, and is a pale yellow powder, melting at 56°. It is decomposed into dinitrophenol and azoimide when boiled with an alkali.

Dinitrophenylhydrazine readily reacts in the characteristic manner with aldehydes and ketones. *Benzylidenedinitrophenylhydrazine*,



forms orange-coloured plates, melting at 235°. *Orthohydroxybenzylidenedinitrophenylhydrazine* crystallises from alcohol in purple-red, slender, matted needles, melting at 248°. *Acetonedinitrophenylhydrazine* forms slender, yellow needles, and melts at 128°. Ethylic acetoacetate also reacts with the hydrazine, forming a *condensation product*,

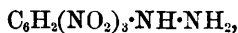


which crystallises from dilute alcohol in deep, orange-yellow prisms, melting at  $96^\circ$ . These compounds are, as a rule, readily decomposed by alkalis, with difficulty by acids.

In order to definitely establish the identity of the derivatives of phenylhydrazine with those prepared directly from hydrazine hydrate, dinitraniline was converted into dinitrophenylhydrazine by means of the diazo-reaction, and was found to be identical in every respect with the synthetical product.

2:4-Dinitrodiazobenzene nitrate forms lustrous, yellowish plates, which explode violently when heated in a test-tube. It reacts with resorcinol to form a colouring matter, dinitrobenzeneazoresorcinol, which is a microcrystalline, dark reddish-brown powder, with a green lustre, and dyes wool and silk a golden-brown.

Picrylic chloride reacts violently with hydrazine hydrate to form picrylhydrazine (1:2:4:6-trinitrophenylhydrazine),



which crystallises in small, hard prisms of a deep, reddish-brown colour. It melts at  $186^\circ$ , and explodes feebly when heated in a tube. It is almost insoluble in benzene, sparingly soluble in cold alcohol, readily in acetic acid. It has a more acid character than the dinitro-compound, does not form salts with acids, and is more readily attacked by alkalis, forming blue solutions. It reduces both Fehling's solution and ammoniacal solutions of silver oxide. Acetylpicrylhydrazine crystallises in greenish-yellow prisms with a silky lustre, and melts at  $223^\circ$ .

Benzylidenepicrylhydrazine crystallises in orange-coloured, matted needles, and melts at  $267^\circ$ . It is insoluble in water and dilute acids, and is decomposed by dilute alkalis. Acetonepicrylhydrazone forms slender, brown needles, melting and decomposing at  $125^\circ$ .

Hydrazine hydrate reacts with paranitrophenylazoimide in a remarkable manner, paranitraniline and a little nitrobenzene being formed, along with nitrogen and ammonia, the chief action occurring according to the equation  $3\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_3 + 3\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} = 3\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + 5\text{N}_2 + 2\text{NH}_3 + 3\text{H}_2\text{O}$ . A similar action takes place between hydrazine hydrate and phenylazoimide, aniline and traces of benzene being formed, in addition to ammonia and nitrogen. Benzoylazoimide, on the other hand, is converted into benzoylhydrazine, azoimide being liberated.

Hydrazine hydrate combines directly with cyanogen to form carbohydrazimine,  $\text{NH}_2 \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{NH}_2$ , which crystallises from dilute alcohol in flat, colourless needles. It is readily soluble in water, and, when heated, decomposes gradually without melting.

This substance contains two hydrazine residues, and therefore reacts with aldehydes and ketones.

Benzylidenecarbohydrazimine,  $\text{C}_2(\text{NH})_2(\text{NH} \cdot \text{N} : \text{CHPh})_2$ , is formed by the direct condensation of carbohydrazimine with benzaldehyde. It crystallises in light, bronze-coloured plates, and melts at  $218^\circ$ .

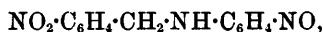
Acetonitrile does not react with hydrazine hydrate in the cold, but at  $150^\circ$  methylhydrazicarbimine,  $\text{NH} : \text{CMe} \cdot \text{NH} \cdot \text{NH} \cdot \text{CMe} \cdot \text{NH}$ , is formed.

It is readily soluble in alcohol, and melts at 197—198°. It does not form condensation products with aldehydes, and does not yield hydrazine when boiled with dilute acids or alkalis, but is decomposed by concentrated potash with evolution of ammonia.

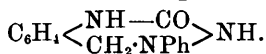
*Phenylhydrazinecarbimine* is obtained from hydrazine hydrate and benzonitrile in a similar manner. It forms colourless, lustrous plates, melts at 250°, and is insoluble in water, dilute acids, and alkalis. Paratolunitrile does not react with hydrazine hydrate under the same conditions. A. H.

**$\alpha$ -Acetylphenylhydrazine.** By O. WIDMAN (*Ber.*, 1894, 27, 2964—2965).—All attempts to prepare  $\alpha$ -acetylphenylhydrazine, by the author's method (*Abstr.*, 1893, i, 411), from  $\beta$ -acetylphenylhydrazine, failed, but Pechmann and Runge's description of its properties (*Abstr.*, 1894, i, 457) has indicated the necessary conditions, and it can be obtained by heating diacetylphenylhydrazine with 10 parts of dilute sulphuric acid (10 per cent.) for 30 minutes at 70—80°. The yield is about 10 per cent. of the diacetyl-derivative employed.  $\alpha$ -Acidylphenylhydrazines are readily distinguished from  $\beta$ -acidyl and  $\alpha\beta$ -diacidyl derivatives, as the latter give Bülcw's reaction and the former do not. J. B. T.

**Orthamidobenzylhydrazines.** By M. BUSCH (*Ber.*, 1894, 27, 2897—2904; compare *Abstr.*, 1892, 734).—*Orthonitrobenzylphenylnitrosamine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NO}$ , is prepared by the action of sodium nitrite on orthonitrobenzylaniline, and crystallises from ether in well-developed, vitreous prisms, melting at 84°. When it is treated in ethereal solution with hydrogen chloride, it undergoes molecular change, and is converted into *orthonitrobenzylnitrosoaniline*,



which forms steel-blue needles, melting at 165—167°. The reduction of the nitrosamine with tin and hydrochloric acid leads to the formation of phenylindazole, with sodium amalgam and alcohol, to orthamidobenzylaniline, and with zinc dust and acetic acid, to *orthamidobenzylphenylhydrazine*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NH}_2$ . The last of these crystallises in vitreous needles, melts at 102°, and is a powerful base. The *oxalate* crystallises in colourless needles, melting at 138°, whilst the salts with mineral acids are deliquescent. Phosgene reacts with the hydrazine base forming a *condensation product* of the formula



This substance separates from acetic acid in compact crystals, melting and decomposing at 281°. Carbon bisulphide reacts with the free base to form the corresponding *thio-derivative*,  $\text{C}_6\text{H}_4\left\langle \begin{array}{c} \text{NH} - \text{CS} \\ \text{CH}_2\cdot\text{NPh} \end{array} \right\rangle \text{NH}$ , which forms compact crystals, and melts and decomposes at 243°. The instability of the ring of seven atoms, which is present in this compound, is shown by the fact that, when the substance is reduced, ammonia is eliminated and phenyltetrahydroquinazoline produced.

Orthamidobenzylphenylhydrazine reacts with benzaldehyde to form a *dibenzylidene compound*,  $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{N}\cdot\text{CHPh}$ , which crystallises in yellow needles, and melts at  $148\text{--}150^\circ$ .

Similar derivatives have been obtained from *orthonitrobenzylparaphenylnitrosamine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , which crystallises in orange-coloured plates and melts at  $95^\circ$ . *Orthamidobenzylphenylhydrazine* forms colourless, rhomboidal tablets, and melts at  $98^\circ$ . The *oxalate* crystallises in slender, white needles. Carbon bisulphide and the base yield a *thiocarbamide* derivative,

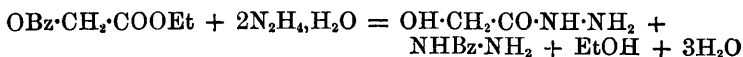


which crystallises in lustrous needles and melts at  $198^\circ$ .

*Dibenzylideneorthamidobenzylparaphenylnhydrazine* crystallises in lemon-yellow prisms, and melts at  $152^\circ$ . A. H.

**Hydrazides and Azides of Organic Acids.** By T. CURTIUS (*J. pr. Chem.*, 1894, [2], 50, 275—294).—The author applies the term *acid hydrazides* to substances of the formula  $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , whilst the derivatives of azoimide are designated by the term *acid azides*, and have the formula  $\text{R}\cdot\text{CO}\cdot\text{N}_3$ .

The acid hydrazides are formed by the action of hydrazine hydrate on the ethereal salts of the organic acids, and the acid amides, chlorides, and azides, whilst the sulphohydrazides may be obtained in a similar manner from the corresponding sulphochlorides. The ethereal salts of the bibasic acids act in the same manner, two hydrazine residues being introduced. The imides and anhydrides of these acids, on the other hand, only react with 1 mol. of hydrazine. The reactions all take place in the cold, some even with explosive violence. The compounds thus produced are crystalline, colourless substances, which have powerful reducing properties, and are soluble in dilute acids. They are stable towards acids and alkalis, although some of the hydrazides of the fatty acids are decomposed by these reagents, with formation of hydrazine and the acid. By the introduction of an acid radicle, the basic character of the hydrazine is weakened to a less extent than that of ammonia, the hydrazides being distinctly basic; they form crystalline and stable salts, which unite with the chlorides of gold and platinum to form double salts, the metallic compound being usually reduced to a lower state of oxidation. One of the hydrogen atoms of the hydrazine residue can be displaced by the alkali metals or by silver; the sodium derivatives are crystalline and hygroscopic. The acid hydrazides yield acetyl derivatives when treated with acetic chloride or anhydride, but the exact constitution of these compounds has not yet been ascertained. The primary hydrazides may also be obtained by the action of hydrazine hydrate on acid derivatives of ethylic glycollate, benzhydrazide having been, first of all, prepared in this way. The reaction is as follows:



glycollic hydrazide being formed, and not hydrazineacetic acid, as

previously supposed. When glycollic hydrazide is heated with water, it is converted into hydraziglycollide,  $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \cdot \text{CH}_2 \end{smallmatrix} > \text{CO}$ . Alkyl derivatives of ethylic glycollate behave towards hydrazine hydrate in the normal manner, the corresponding alkyl glycollic hydrazide being obtained.

All the primary hydrazides react with aldehydes and ketones to produce colourless condensation products, generally sparingly soluble.

The secondary symmetrical hydrazides are formed when hydrazine hydrate is acted on with an excess of an ethereal salt of an organic acid, or when the latter substance is added to a primary hydrazide. They are also produced by the oxidation of the primary hydrazides by means of iodine or mercuric oxide, and when the primary hydrazides are heated for some time above their melting points, hydrazine being eliminated, generally in the form of ammonia and nitrogen. The hydrazides of the bibasic acids behave in a similar manner, oxalhydrazide,  $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , for example, yielding a dioxalhydrazide, which probably has the constitution  $\text{CO} < \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{CO}$ .

The secondary symmetrical hydrazides are colourless substances of high melting point, and have faintly basic properties. They are even more stable towards acids than the primary compounds, and do not react with aldehydes and ketones.

*Action of Nitrous acid on Acid Hydrazides.*—The primary acid hydrazides are usually converted into acid azides by the action of nitrous acid, nitroso-compounds being most probably formed as intermediate products. The hydrazides of the bibasic acids, with the exception of fumaric and carbonic acids, however, yield no acid azide, but are converted into substances which are identical with the products obtained by the action of oxidising agents on them. The acid azides may also be prepared by the action of nitric acid on the hydrazides, or by treating these with aqueous diazobenzene sulphate (Abstr., 1893, i, 463). Benzoylazoimide,  $\text{Bz} \cdot \text{N}_3$ , and the azides of the substituted benzoic acids, melt at low temperatures, and decompose more or less violently when heated considerably above their melting points. They are poisonous, have no decided acid or basic properties, and are converted by warming with acids or bases into azoimide and the corresponding acid. Reducing agents either decompose the azides into azoimide and the corresponding acid, which then undergoes secondary changes (alcoholic ammonium sulphide, alcohol and sodium amalgam), or convert them into nitrogen and the corresponding acid amide,  $\text{Bz} \cdot \text{N}_3 + \text{H}_2 = \text{Bz} \cdot \text{NH}_2 + \text{N}_2$  (acid reducing agents), or act on two molecules, which unite to form a secondary hydrazine, two-thirds of the nitrogen being evolved in the form of gas,  $2\text{Bz} \cdot \text{N}_3 + \text{H}_2 = \text{Bz} \cdot \text{NH} \cdot \text{NH} \cdot \text{Bz} + 2\text{N}_2$  (energetic reduction in alkaline solution).

The azides are completely decomposed if boiled with water for some time. Benzoylazoimide, for example, is thus quantitatively decomposed according to the equation  $2\text{Bz} \cdot \text{N}_3 + \text{H}_2\text{O} = 2\text{N}_2 + \text{CO}_2 + \text{CO}(\text{NHPh})_2$ . When boiled with alcohol, a similar change occurs, urethanes being formed (Abstr., 1894, i, 331). Similar changes are produced by bromine, which converts benzoylazoimide into

bromocarbani and nitrogen,  $\text{BzN}_3 + \text{Br}_2 = \text{CO:NPhBr}_2 + \text{N}_2$ , and by hydrogen chloride in ethereal solution, hippurazide being thus converted into hippurocarbani hydrochloride,  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3 + \text{HCl} = \text{N}_2 + \text{NHBz}\cdot\text{CH}_2\cdot\text{N}(\text{CO})\text{HCl}$ . The compound previously described as diazohippuramide is actually hippurazide,



Aniline, in ethereal solution, decomposes the acid azides, with liberation of azoimide and formation of the anilide of the organic acid, whilst an excess of aniline, when heated with benzazide, yields diphenylcarbamide and nitrogen. The hydrazides in ethereal solution act in the same way as aniline under the same circumstances, azoimide and a substituted hydrazine being obtained, whilst in solution in acetone they always produce molecular change, accompanied by evolution of nitrogen,

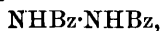


Of the acid hydrazides of the bibasic acids, those of fumaric and carbonic acids behave towards nitrous acid in a similar manner to the hydrazides of the monobasic acids. Fumarhydrazide is thus converted into a frightfully explosive diazide,  $\text{C}_2\text{H}_2(\text{CO}\cdot\text{N}_3)_2$ , and carbohydrazide into carbazide,  $\text{CO}(\text{N}_3)_2$ , which is a crystalline, spontaneously explosive substance.

An account of the experimental researches, of the results of which the foregoing is a general statement, will be shortly published.

A. H.

**Benzoylhydrazine (Benzhydrazide).** By G. STRUVE (*J. pr. Chem.*, 1894, [2], 50, 295—310; compare the foregoing abstract). —Benzoylhydrazine,  $\text{NHBz}\cdot\text{NH}_2$ , which was first prepared by Curtius from ethylic benzoylglycollate (*Abstr.*, 1891, 56), may also be obtained by the action of hydrazine hydrate on ethylic benzoate, benzamide, benzoic chloride, or benzoylazoimide,  $\text{BzN}_3$ . It forms colourless plates with a silvery lustre, and melts at  $112.5^\circ$ . It reduces Fehling's solution, and ammoniacal silver solution in the cold, and converts platonic chloride into the platinous salt. It is very slowly attacked by dilute acids, and is still more stable towards alkalis. When rapidly heated, it boils without decomposing, but when heated for some time at  $180^\circ$  it decomposes with evolution of gas and formation of dibenzoylhydrazine. The *hydrochloride*,  $\text{NHBz}\cdot\text{NH}_2\cdot\text{HCl}$ , forms small, colourless tablets, which readily dissolve in water and alcohol, and melt and decompose at about  $185^\circ$ . The *platinosochloride*  $(\text{NHBz}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_4$ , is obtained as a yellowish-white precipitate when platinous chloride is added to an alcoholic solution of benzoylhydrazine, nitrogen being evolved; it is decomposed by boiling water. *Sodium benzoylhydrazine*, prepared by the action of sodium on benzoylhydrazine suspended in xylene, or by that of sodium ethoxide on its alcoholic solution, crystallises in tablets, which are stable in the air. *Acetylbenzoylhydrazine*,  $\text{N}_2\text{H}_2\text{BzAc}$ , crystallises in colourless, lustrous plates, melting at  $170^\circ$ . Symmetrical dibenzoylhydrazine,





has been previously described by Curtius (Abstr., 1891, 56). It is formed when benzoylhydrazine is heated at  $180^{\circ}$ , by the action of ethylic benzoate on the hydrazide, and by the action of iodine or mercuric oxide on an alcoholic solution of the same substance. It crystallises in small, silky needles, melting at  $233^{\circ}$ . By continued boiling with dilute sulphuric acid, it is converted into benzoic acid and hydrazine sulphate.

The compounds of benzoylhydrazine with aldehydes are formed by shaking the hydrazine with the aldehyde in aqueous solution, and are scarcely soluble in water. They are insoluble in dilute acids and alkalis, but are decomposed by boiling with them. *Benzylidenebenzoylhydrazine*,  $\text{CHPh}\cdot\text{N}\cdot\text{NHBz}$ , crystallises in colourless needles, melting at  $202^{\circ}$ . *Orthohydroxybenzylidenebenzoylhydrazine* forms yellowish-white needles, melting at  $182^{\circ}$ . *Metanitrobenzylidenebenzoylhydrazine* crystallises in well-developed prisms, which become red on exposure to the air, and melt at  $192^{\circ}$ . *Parahydroxybenzylidenebenzoylhydrazine* forms fascicular groups of colourless needles, melting at  $233^{\circ}$ . *Cinnamylidenebenzoylhydrazine* crystallises in small, colourless needles, and melts at  $193^{\circ}$ . *Propylidenebenzoylhydrazine* is readily soluble in hot water, and forms colourless prisms, which melt at  $117^{\circ}$ . Benzoylhydrazine does not appear to react with glucose.

The compounds of benzoylhydrazine with ketonic substances resemble the aldehydo-compounds in their general properties. The reaction with orthodiketones only proceeds when the two are heated together under pressure; and whilst the  $\alpha$ -ketonic acids react very easily, no definite compounds have yet been obtained from the  $\beta$ - and  $\gamma$ -acids. *Acetonebenzoylhydrazone* forms colourless needles, melting at  $142^{\circ}$ . *Benzylideneacetonebenzoylhydrazone* crystallises in silky needles, and melts at  $157^{\circ}$ . *Acetophenonebenzoylhydrazone* forms colourless needles, and melts at  $153^{\circ}$ . Benzoylhydrazine reacts with isatin, forming a condensation product,  $\text{NHBz}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{smallmatrix} \text{N}$ , which crystallises in lustrous, golden-yellow plates, and melts at  $279^{\circ}$ .

With benzile, a *dihydrazone*,  $\text{NHBz}\cdot\text{N}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{NHBz}$ , is formed which crystallises in small, colourless needles melting at  $206^{\circ}$ . The *benzoylhydrazone of ethylic pyruvate* also crystallises in colourless needles, and melts at  $155^{\circ}$ .  
A. H.

**Action of Nitrous Acid on Isomethyleugenol.** By G. MALAGNINI (*Gazzetta*, 1894, 24, ii, 1—20; compare Abstr., 1893, i, 196).—

*Diisonitrosoisomethyleugenol peroxide*,  $\text{MeC} \begin{smallmatrix} \text{C}=\text{N} \\ \text{O} \end{smallmatrix} \cdot \text{O} \cdot \text{C} \begin{smallmatrix} \text{C}=\text{N} \\ \text{O} \end{smallmatrix} \cdot \text{NO}_2 \cdot \text{C}_6\text{H}_4(\text{OMe})_2$ , is prepared by treating diisonitrosoisomethyleugenol peroxide with nitric acid; it separates on pouring the product into water, and crystallises in straw-coloured needles melting at about  $189^{\circ}$ .

The *bromo-derivative* of the peroxide,  $\text{C}_6\text{H}_4\text{Br}(\text{OMe})_2 \cdot \text{C} \begin{smallmatrix} \text{C}=\text{N} \\ \text{O} \end{smallmatrix} \cdot \text{O} \cdot \text{C} \begin{smallmatrix} \text{C}=\text{N} \\ \text{O} \end{smallmatrix} \cdot \text{O}$ , obtained by brominating the peroxide in glacial acetic acid solution, forms small, colourless crystals, melting at  $133^{\circ}$ .

Diisonitrosoisomethyleugenol peroxide, like the corresponding iso-

safrole compound, yields an *isomeride*,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \overset{\text{C}(\text{NOH}) \cdot \text{CH}_2}{\underset{\text{C}=\text{N}-\text{O}}{\text{C}}}$ , on warming with potash; it separates from ethylic acetate in colourless crystals, melting and decomposing at  $171-172^\circ$ ; it is very soluble in aqueous potash, whereas the peroxide is insoluble. The *monacetyl*-derivative crystallises in white needles melting at  $115^\circ$ .

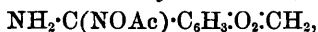
The peroxide is reduced by tin and hydrochloric acid, with formation of a *furazanic* compound,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \overset{\text{MeC}=\text{N}}{\underset{\text{C}=\text{N}}{\text{C}}} > \text{O}$ ; this crystallises in stellate aggregates, melts at  $75^\circ$ , and is very stable. On reducing the peroxide with zinc-dust and acetic acid, the  $\alpha$ -dioxime,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{C}(\text{NOH}) \cdot \text{CMe} \cdot \text{NOH}$ , is obtained; the crystals melt at  $112^\circ$ , and effloresce on exposure to air. When heated for some time at a temperature a little above  $112^\circ$ , they are transformed into the  $\beta$ -dioxime; this melts at  $196^\circ$ , and resembles the  $\alpha$ -compound in appearance.

The *monacetyl* derivative of the  $\alpha$ -dioxime crystallises in colourless prisms melting at  $98^\circ$ , and yields the furazanic compound described above on heating with potash. The *acetyl* derivative of the  $\beta$ -dioxime melts at  $105^\circ$ , and when treated with potash is hydrolysed with regeneration of the oxime. Both the  $\alpha$ - and  $\beta$ -dioximes yield diisositroisomethylengenol peroxide on oxidation with potassium ferricyanide in alkaline solution.

*Isomethyleugenol nitrosite*,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \overset{\text{MeCH} \cdot \text{N}-\text{O}}{\underset{\text{CH} \cdot \text{N}-\text{O}}{\text{C}}} > \text{O}$ , may be prepared by gradually adding dilute sulphuric acid, a few drops at a time, to a light-petroleum solution of isomethyleugenol suspended in sodium nitrite solution. It melts and decomposes at  $107^\circ$ , and is very unstable; on boiling with alcohol, it is converted into diisositroisomethyleugenol peroxide, melting at  $118^\circ$ . W. J. P.

**Configuration of Certain Glyoximes.** By A. ANGELI and G. MALAGNINI (*Gazzetta*, 1894, **24**, ii, 131—145).—Isosafrole- $\alpha$ -dioxime is very readily acted on by phosphorus oxychloride, yielding an *azoxime*,  $\text{CMe} \cdot \text{N} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \text{---N} > \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 \cdot \text{CH}_2$ , which forms almost colourless crystals melting at  $116-117^\circ$ ; it is insoluble in potash, and has an odour resembling that of coumarin.

On heating piperonylonitrile in a sealed tube at  $110^\circ$  with hydroxylamine hydrochloride and sodium carbonate, an *amidoxime*,  $\text{NH}_2 \cdot \text{C}(\text{NOH}) \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 \cdot \text{CH}_2$ , is obtained; it crystallises in thin, yellow needles melting at  $143^\circ$ . The *acetyl* derivative,



is a colourless, crystalline substance, which melts at  $128^\circ$ ; on heating it just above its melting point, it is converted into the azoxime described above.

Isosafrole  $\alpha$ -dioxime, on treatment with phosphorus pentachloride, yields the azoxime, together with *acetylpiperylcarbamide*,



the latter crystallises in long, white needles melting at about  $216^{\circ}$ , and, on boiling with potash, yields ammonia and acetic acid.

Isosafrole- $\beta$ -dioxime, when treated with phosphorus oxychloride, yields the azoxime melting at  $116$ – $117^{\circ}$ , together with piperonylnitrile. The same products are formed on treating the  $\beta$ -dioxime with phosphorus pentachloride.

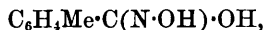
On warming the diacetyl-derivative of isosafrole- $\alpha$ -dioxime with potash, the furazanic compound obtained from isosafrole is formed; under similar conditions, the diacetyl-derivative of the  $\beta$ -dioxime is converted into the  $\beta$ -dioxime.

On heating isosafrole- $\alpha$ -dioxime in a closed tube with water at  $160^{\circ}$  for three hours, it is completely converted into the above-mentioned furazanic compound; the  $\beta$ -dioxime, when treated in like manner, yields the furazan together with the  $\alpha$ -dioxime.

The results described above demonstrate that the  $\alpha$ - and  $\beta$ -dioximes of isosafrole are compounds of the same type as the  $\gamma$ - and  $\alpha$ -benzile-dioximes respectively.

W. J. P.

**Occurrence of Polymorphous Modifications of Derivatives of Hydroxylamine.** By W. LOSSEN\* (*Annalen*, 1894, **281**, 169–305; compare Abstr., 1892, 711).—*Metatoluhydroxamic acid*,



is obtained, together with metatoluic acid and mono- and dihydroxamic acids, by the interaction of hydroxylamine hydrochloride, metatoluic chloride, and soda; it forms orthorhombic crystals, melting at  $119$ – $120^{\circ}$ ;  $a:b:c = 0.5381:1:0.2908$ . The *para*-isomeride is prepared in a similar manner, and crystallises in colourless, pearly, orthorhombic leaflets, melting and decomposing at  $148^{\circ}$ ;  $a:b = 0.9325:1$ .

*Isophthalylhydroxamic acid*,  $\text{C}_6\text{H}_4[\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}]_2$ , prepared from isophthalic chloride, crystallises in spherical aggregates, melting at  $192^{\circ}$  with decomposition. The isomeric *terephthalylhydroxamic acid* crystallises in prisms melting and decomposing at  $232^{\circ}$ ; its sodium salt,  $\text{C}_8\text{H}_6\text{N}_2\text{O}_4\text{Na}_2\cdot 2\text{H}_2\text{O}$ , is obtained in microscopic, flattened prisms, and explodes on heating. The potassium hydrogen salt,  $\text{C}_8\text{H}_7\text{N}_2\text{O}_4\text{K}$ , is also crystalline and explosive; the barium salt is insoluble in water, and, when carefully distilled to avoid explosion, yields a small proportion of paraphenylenediamine.

Alkyl salts of the mono-substituted hydroxamic acids, in which the alkyl radicle enters the oximido-group, may be prepared by three methods. By the action of an alkyl iodide on an alkali salt of the hydroxamic acid; by the action of an acid chloride on an alkylhydroxylamine; or by the hydrolysis of an alkyl alkylhydroxamate—the latter method seems to yield the best results. The potassium derivative,  $\text{OEt}\cdot\text{N}\cdot\text{CPh}\cdot\text{OK}$ , of ethyl benzhydroxamate is described, together with the corresponding sodium, barium, magnesium, and copper compounds. Methyl benzhydroxamate is conveniently prepared by the interaction of benzhydroxamic acid and methyl

\* The nomenclature of the hydroxamic acids is in a state of great confusion; the names in the abstract are those given in the original paper.—EDITORS.

iodide in a methylic alcohol solution of potash; it crystallises in orthorhombic plates;  $a : b = 0.924 : 1$ .

*Ethylic paratoluhydroxamate*,  $C_6H_4Me \cdot C(N \cdot OEt) \cdot OH$ , may be prepared from paratolenylethoximidoethylic ether from ethylic ethylparatoluhydroxamate; or from paratoluethylbenzhydroxylamine; it crystallises in orthorhombic prisms melting at  $101^\circ$ ;  $a : b : c = 0.5642 : 1 : 0.7212$ .

Ethylic anishydroxamate is obtained in mono-symmetric crystals;  $a : b : c = 1.3174 : 1 : 0.8563$ .  $\beta = 86^\circ 54'$ . Its *benzylic* derivative,  $OMe \cdot C_6H_4 \cdot C(N \cdot OC_2H_5) \cdot OH$ , forms monosymmetric crystals melting at  $113^\circ$ ;  $a : b : c = 0.9314 : 1 : 0.8231$ .  $\beta = 85^\circ 10'$ .

$\alpha$ -Ethylbenzhydroxamic acid is obtained by the action of potash on ethylic  $\alpha$ -benzoparatoluhydroxamate, or of alcoholic ammonia on ethylic  $\alpha$ -ethylbenzhydroxamate; the  $\beta$ -ethylbenzhydroxamic acid is formed from the corresponding  $\beta$ -isomerides of these substances. By treating  $\alpha$ - or  $\beta$ -ethylbenzhydroxamic acid with paratoluic chloride, ethylic  $\alpha$ - or  $\beta$ -benzoparatoluhydroxamate respectively is produced. It seems not improbable that a third modification of ethylbenzhydroxamic acid can exist; an *isomeride*, melting at about  $40^\circ$ , is obtained in small quantities as a bye-product in several processes.

The methylbenzhydroxamic acid, which melts at  $64$ – $65^\circ$ , described by Lossen and Zanni (*Annalen*, 182, 226), is termed the  $\alpha$ -modification; all attempts to prepare it again have failed, but it nevertheless exists, and seems to crystallise in the orthorhombic system. Its  $\beta$ -isomeride, which melts at  $101^\circ$ , may be prepared in many ways; it crystallises in large, lustrous, cubic crystals, showing pentagonal hemihedrism; its *hydrochloride* is a crystalline powder.

The  $\alpha$ - and  $\beta$ -propylbenzhydroxamic acids,  $OH \cdot N \cdot CPh \cdot OC_3H_7$ , are obtained at the same time when benzimidopropylic ether acts on hydroxylamine hydrochloride. The  $\alpha$ -acid crystallises in lustrous, monosymmetric prisms, melting at  $33.5^\circ$ ;  $a : b : c = 2.090 : 1 : 2.133$ ;  $\beta = 93^\circ 3'$ . The  $\beta$ -acid is obtained in anorthic prisms, melting at  $47.5$ – $48^\circ$ ;  $\gamma = 76^\circ 58'$ .

An oily *ethylmetatoluhydroxamic acid* is obtained by treating ethylic dimetatoluhydroxamate with potash.

The  $\alpha$ - and  $\beta$ -ethylparatoluhydroxamic acids,  $C_6H_4Me \cdot C(N \cdot OH) \cdot OEt$ , may be prepared by several methods. The  $\alpha$ -acid is obtained crystalline with difficulty, and melts at  $34^\circ$ ; its *hydrochloride* was prepared. The  $\beta$ -acid crystallises in large, anorthic tablets or prisms, melting at  $103^\circ$ ;  $a : b : c = 0.797 : 1 : 0.459$ .  $\alpha = 93^\circ 1'$ ;  $\beta = 101^\circ 53'$ ;  $\gamma = 88^\circ 56'$ .

The  $\alpha$ - and  $\beta$ -ethylanishydroxamic acids,  $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot OEt$ , may be prepared in several ways; the  $\alpha$ -acid crystallises in thin, monosymmetric plates melting at  $49^\circ$ . The  $\beta$ -isomeride crystallises in monosymmetric needles;  $a : b : c = 1.4693 : 1 : 1.4043$ .  $\beta = 72^\circ 27.5'$ . It melts at  $97^\circ$ .

*Methylanishydroxamic acid*,  $OMe \cdot C_6H_4 \cdot C(N \cdot OH) \cdot OMe$ , crystallises well, and melts at  $113.5^\circ$ .

The same methylic salt is obtained from both  $\alpha$ - and  $\beta$ -ethylbenzhydroxamate; it melts at  $151^\circ$ . *Methylic methylbenzhydroxamate* is a highly refractive liquid boiling at  $216$ – $217^\circ$ .

*Ethylic ethylparatoluhydroxamate* is obtained as a mobile oil, boiling at 150—155° under a low pressure; the *methylic* salt and *ethylic methylanishydroxamate* were also prepared.

*Dimetatoluhydroxamic acid*,  $C_7H_7 \cdot C(NO \cdot CO \cdot C_2H_5) \cdot OH$ , is obtained during the preparation of metatoluhydroxamic acid; it crystallises in monosymmetric tablets;  $a : b : c = 0.8201 : 1 : 1.3871$ .  $\beta = 108^\circ 45'$ . It melts at  $95.5^\circ$ . The *ethylic* salt is an oily liquid, having a sp. gr. of 1.1160 at  $15^\circ$ . The isomeric *dipara-acid* crystallises in monosymmetric pyramids melting at  $167^\circ$ ;  $a : b : c = 1.3554 : 1 : 3.1580$ .  $\beta = 87^\circ 53.5'$ . The  $\alpha$ -*ethylic* salt is prepared from the silver salt, and crystallises in anorthic plates or prisms melting at  $78^\circ$ ;  $a : b : c = 0.9059 : 1 : 1.2160$ .  $\alpha = 80^\circ 52'$ ;  $\beta = 101^\circ 1'$ ;  $\gamma = 110^\circ 10'$ . An isomeric  $\beta$ -*ethylic* salt is obtained by the action of paratoluic chloride on  $\alpha$ - or  $\beta$ -ethylparatoluhydroxamic acid; it crystallises in monosymmetric plates melting at  $54^\circ$ . Both salts yield the acid on hydrolysis with hydrochloric acid.

*Benzparatoluhydroxamic acid*,  $OH \cdot CPh \cdot NO \cdot CO \cdot C_2H_5$ , is prepared by hydrolysis of its  $\alpha$ - or  $\beta$ -*ethylic* salt or by the action of paratoluic chloride on benzhydroxamic acid; it forms monosymmetric tablets melting at  $155^\circ$ .  $a : b : c = 1.4312 : 1 : 2.2083$ .  $\beta = 65^\circ 25'$ . The  $\alpha$ -*ethylic* salt is obtained from the silver salt or by the action of paratoluic chloride on  $\alpha$ -ethylbenzhydroxamic acid; it forms anorthic crystals melting at  $114.5^\circ$ ;  $a : b : c = 0.8494 : 1 : 1.0058$ .  $\alpha = 88^\circ 23.5'$ ;  $\beta = 101^\circ 35'$ ;  $\gamma = 119^\circ 3'$ . The  $\beta$ -*ethylic* salt, prepared from  $\beta$ -ethylbenzhydroxamic acid, crystallises in monosymmetric tablets melting at  $70^\circ$ ;  $a : b : c = 1.0882 : 1 : 0.6851$ .  $\beta = 84^\circ 35'$ .

*Paratolubenzhydroxamic acid*,  $C_7H_7 \cdot C(NO \cdot CPh) \cdot OH$ , melts at  $156^\circ$ . The  $\alpha$ -*ethylic* salt, prepared from the silver salt or from  $\alpha$ -ethylparatoluhydroxamic acid, forms monosymmetric crystals melting at  $62^\circ$ ;  $a : b = 1.3040 : 1$ .  $\beta = 68^\circ 23'$ . The  $\beta$ -*isomeride*, prepared from  $\beta$ -ethylparatoluhydroxamic acid, is also monosymmetric, and melts at  $51.5$ — $52^\circ$ ;  $a : b : c = 1.0766 : 1 : 1.8364$ .  $\beta = 83^\circ 50'$ . A third  $\gamma$ -*isomeride*, melting at  $56^\circ$ , accompanies the  $\alpha$ -salt; the oily residue obtained after separation of this, together with the solid salts, yields  $\beta$ -ethylparatoluhydroxamic acid on treatment with potash.

*Isophthalylbenzhydroxamic acid*,  $C_6H_4[C(NO \cdot CPh) \cdot OH]_2$ , prepared from benzoic chloride and isophthalylhydroxamic acid, crystallises in white needles melting at  $162^\circ$ ; the *potassium* salt,  $C_{22}H_{14}N_2O_6K_2$ , is readily converted into metaphenylenecarbamide in aqueous solution. The isomeric *terephthalylbenzhydroxamic acid* crystallises in leaflets melting at  $198^\circ$ ; its *potassium* salt is readily hydrolysed with formation of paraphenylenecarbamide.

Dibenzhydroxamic acid is formed by the action of dry hydrogen chloride on benzhydroxamic acid; the fact explains the formation of the former acid during the decomposition of the hydrochlorides of alkylhydroxamic acids. Both  $\alpha$ - and  $\beta$ -*ethylic* dibenzhydroxamate have the normal molecular weight in freezing phenol. The oily product of the action of methylic iodide on silver dibenzhydroxamate, which has previously been considered as the methylic salt, yields a crystalline  $\alpha$ -*methylic dibenzhydroxamate* by suitable treatment; the salt crystallises in orthorhombic prisms melting at  $53$ — $54^\circ$ ;  $a : b =$

0.9713 : 1. The  $\beta$ -methylic salt is obtained by the action of benzoic chloride on  $\beta$ -methylbenzhydroxamic acid; it forms anorthic crystals melting at  $55.3^\circ$ ;  $a : b : c = 1.6108 : 1 : 0.7226$ .  $\alpha = 115^\circ 24'$ ;  $\beta = 112^\circ 41'$ ;  $\gamma = 76^\circ 10'$ . The two salts yield  $\beta$ -methylbenzhydroxamic acid on hydrolysis. The  $\alpha$ -propylic salt, prepared by the action of propylic iodide on silver dibenzhydroxamate, crystallises in orthorhombic prisms melting at  $32^\circ$ . It is accompanied by the  $\gamma$ -propylic salt (?) which melts at  $20.5$ — $24^\circ$ .  $\beta$ -Propylic dibenzhydroxamate is prepared from propylbenzhydroxamic acid; it crystallises in the anorthic system, and melts at  $50.3^\circ$ ;  $a : b : c = 1.9767 : 1 : 0.7758$ .  $\alpha = 90^\circ 52'$ ;  $\beta = 98^\circ 8'$ ;  $\gamma = 84^\circ 33'$ . All three isomerides yield  $\beta$ -propylbenzhydroxamic acid on hydrolysis.

$\alpha$ -Ethylic benzparatoluhydroxamate,  $\text{CPh}\cdot\text{C}(\text{NO}\cdot\text{CO}\cdot\text{C}_7\text{H}_7)\cdot\text{OEt}$ , prepared by methods similar to those employed for the preceding  $\alpha$ -salt, crystallises in the anorthic system, and melts at  $114.5^\circ$ ;  $a : b : c = 0.8494 : 1 : 1.0058$ .  $\alpha = 88^\circ 23.5'$ ;  $\beta = 101^\circ 35'$ ;  $\gamma = 119^\circ 3'$ .

The  $\beta$ -isomeride crystallises in monosymmetric tablets melting at  $70^\circ$ ;  $a : b : c = 1.0882 : 1 : 0.6851$ .  $\beta = 84^\circ 35'$ . The salts yield benzparatoluhydroxamic acid on acid hydrolysis, and  $\alpha$ - and  $\beta$ -ethylbenzhydroxamic acid respectively on hydrolysis with potash. The  $\alpha$ -methylic salt crystallises in the anorthic system, and is crystallographically similar to the  $\alpha$ -ethylic salt; it melts at  $108.5^\circ$ ;  $a : b : c = 0.8006 : 1 : 1.0756$ .  $\alpha = 86^\circ 8.5'$ ;  $\beta = 99^\circ 10'$ ;  $\gamma = 120^\circ 19.5'$ . The  $\beta$ -methylic salt is also anorthic, and melts at  $65^\circ$ ;  $a : b = 1.4907 : 1$ .  $\alpha = 104^\circ 25'$ ;  $\beta = 113^\circ 50'$ ;  $\gamma = 96^\circ 23'$ .

$\alpha$ -Ethylic paratolubenzhydroxamate,  $\text{C}_7\text{H}_7\cdot\text{C}(\text{NO}\cdot\text{COPh})\text{OEt}$ , crystallises in monosymmetric prisms melting at  $62^\circ$ ;  $a : b = 1.3040 : 1$ .  $\beta = 68^\circ 22'$ . The  $\beta$ -salt forms monoclinic crystals,  $a : b : c = 1.0766 : 1 : 1.8364$ .  $\beta = 83^\circ 50'$ . It melts at  $51.5$ — $52^\circ$ . The  $\gamma$ -salt melts at  $56^\circ$ , and is separated from an oily residue which has the same composition.

$\alpha$ -Ethylic dianishhydroxamate,  $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{C}(\text{NO}\cdot\text{CO}\cdot\text{C}_7\text{H}_7\text{O})\text{OEt}$ , crystallises in orthorhombic prisms melting at  $94^\circ$ ;

$$a : b : c = 0.8820 : 1 : 0.3970.$$

The  $\beta$ -salt is obtained in anorthic crystals melting at  $77^\circ$ ;  $a : b : c = 0.5971 : 1 : 1.2595$ .  $\alpha = 89^\circ 4'$ ;  $\beta = 100^\circ 43'$ ;  $\gamma = 128^\circ 45'$ . The  $\alpha$ -methylic salt forms orthorhombic leaflets melting at  $50$ — $51^\circ$ , whilst the  $\beta$ -isomeride crystallises in needles melting at  $91^\circ$ .

$\alpha$ -Ethylic anisbenzhydroxamate,  $\text{C}_7\text{H}_7\cdot\text{O}\cdot\text{C}(\text{NO}\cdot\text{COPh})\cdot\text{OEt}$ , forms anorthic crystals melting at  $79^\circ$  (*Annalen*, 217, 7);  $a : c = 1 : 0.7234$ .  $\alpha = 109^\circ 29.5'$ ;  $\beta = 124^\circ 14'$ ;  $\gamma = 62^\circ 23.5'$ . The  $\beta$ -isomeride crystallises in monosymmetric tablets melting at  $51^\circ$ ;  $a : b : c = 0.6009 : 1 : 0.3302$ .  $\beta = 89^\circ 7.5'$ . The  $\alpha$ -methylic salt, prepared from the silver salt, crystallises in monosymmetric tablets melting at  $96^\circ$ ;  $a : b : c = 1.0304 : 1 : 0.8644$ .  $\beta = 85^\circ 54.5'$ . It is accompanied by the  $\beta$ -isomeride, which crystallises in needles melting at  $89^\circ$ .

The following seven derivatives are obtained by the action of acid chlorides on the metallic derivatives of the alkylic salts of substituted hydroxamic acids.

Benzethylacethydroxylamine,  $\text{CPh}(\text{NOEt})\cdot\text{OAc}$ , prepared from acetic chloride and ethylic argentobenzhydroxamate, crystallises

in prisms melting at  $55^{\circ}$ ; it yields ethylic benzhydroxamate on hydrolysis with baryta.

*Benzethylcarbethoxyhydroxylamine*,  $\text{CPh}(\text{N}\cdot\text{OEt})\text{O}\cdot\text{COOEt}$ , prepared by the action of ethylic chlorocarbonate on ethylic potassio-benzhydroxamate, crystallises in plates melting at  $40^{\circ}$ .

*Benzethylsuccinylhydroxylamine*,  $\text{C}_2\text{H}_4(\text{COO}\cdot\text{CPh}\cdot\text{NOEt})_2$ , crystallises in plates melting at  $60^{\circ}$ ; it yields succinic acid on hydrolysis, and on heating above its melting point yields phenylic cyanate and ethylic succinate.

*Benzethylphthalhydroxylamine*,  $\text{C}_6\text{H}_4(\text{COO}\cdot\text{CPh}\cdot\text{NOEt})_2$ , crystallises in prisms melting at  $54^{\circ}$ .

*Benzethylparatoluhydroxylamine*,  $\text{CPh}(\text{NOEt})\text{O}\cdot\text{CO}\cdot\text{C}_7\text{H}_7$ , and *para-toluethylbenzhydroxylamine* are obtained as viscid liquids. *Para-toluethyltoluhydroxylamine* crystallises in the orthorhombic system, and melts at  $70\cdot5^{\circ}$ ;  $a:b:c = 0\cdot6805:1:0\cdot7604$ .

The following triacidylhydroxylamines have the normal molecular weight in freezing phenol solution.

$\gamma$ -Tribenzhydroxylamine (compare *Annalen*, **186**, 35) crystallises in the monosymmetric system;  $a:b:c = 0\cdot9366:1:1\cdot4855$ .  $\beta = 65^{\circ} 33'$ . The  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomerides all give the same benzhydroxamic acid with alcoholic ammonia and the same dibenzhydroxamic acid on hydrolysis with hydrochloric acid; they also all three yield benzoic anhydride and phenylic cyanate on heating. If the heating is too prolonged, benzanilide is formed by the action of the phenylic cyanate on the benzoic anhydride. The  $\alpha$ - and  $\gamma$ -modifications are converted into the  $\beta$ -isomeride on warming with hydrochloric acid. The three isomerides yield *ammonium hydrogen benzhydroxamate*,  $\text{C}_7\text{H}_5\text{NO}_2\cdot\text{NH}_4\cdot\text{C}_7\text{H}_7\text{NO}_2$ , on treatment with alcoholic ammonia; this crystallises well, melts at  $146^{\circ}$ , is very characteristic, and loses ammonia over sulphuric acid or at  $100^{\circ}$ .

$\alpha$ -Dibenzparatoluhydroxylamine,  $\text{C}_7\text{H}_7\cdot\text{COO}\cdot\text{CPh}\cdot\text{NO}\cdot\text{COPh}$ , is prepared by the action of paratoluic chloride on silver dibenzhydroxamate; it crystallises in monosymmetric needles melting at  $131\cdot5^{\circ}$ , and is crystallographically similar to  $\alpha$ -tribenzhydroxylamine;  $a:b:c = 1\cdot4127:1:1\cdot1326$ .  $\beta = 81^{\circ} 36\cdot5'$ . It is accompanied by a  $\beta$ -isomeride (?), which melts at  $104^{\circ}$ .

Isomerides of the following amidoximes could not be prepared.

Benzenylamidoxime methylic ether (compare *Abstr.*, 1889, 1064) crystallises in the monosymmetric system;  $a:b:c = 2\cdot717:1:2\cdot116$ .  $\beta = 121^{\circ} 52'$ . The corresponding *propylic ether*,  $\text{CPh}(\text{NO}\cdot\text{C}_3\text{H}_7)\text{NH}_2$ , prepared by the action of sodium propoxide and propylic iodide on benzenylamidoxime, is crystallographically similar to the preceding, and melts at  $27^{\circ}$ .

Paratolenylamidoxime ethylic ether (compare Schubart, *Abstr.*, 1890, 47) is monosymmetric;  $a:b:c = 0\cdot539:1:0\cdot272$ .  $\beta = 69^{\circ}$ . The corresponding methylic ether is also monosymmetric.

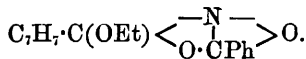
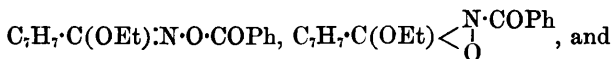
Aniserylamidoxime ethylic ether (compare Miller, *Abstr.*, 1890, 144) is obtained in monosymmetric crystals;

$$a:b:c = 0\cdot8080:1:0\cdot9357. \quad \beta = 86^{\circ} 9'.$$

The above results show that the only classes of hydroxylamine-

derivatives readily obtained in polymorphous modifications, are the alkylhydroxamic acids, the alkylic dihydroxamates, and the triacidylhydroxylamines; polymorphism may be regarded as a general property of these substances. Polymorphism is never observed amongst the hydroxamic acids, the alkylic hydroxamates or the dihydroxamic acids. These substances may be prepared by a number of different methods—thus, the same benzhydroxamic acid is obtained from  $\alpha$ - and  $\beta$ -ethylbenzhydroxamic acid, and from the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -tribenzhydroxylamines—the probability of the occurrence of polymorphism amongst these substances is therefore very small. It would also seem that alkylic acidylhydroxamates only occur in one modification, although here the experimental evidence is not so extensive as in the preceding cases. In certain classes three modifications of some of the substances may be obtained; it may consequently be supposed that each of these substances is trimorphous, although whether this also holds for those groups in which not more than two modifications have been observed is of course still uncertain. The crystallographic examination of compounds of the same type shows that there is in many cases a great similarity between them; no conclusions of importance, however, can be drawn from this fact.

After referring to Hantzsch and Werner's stereochemical hypothesis (Abstr., 1892, 461), the author points out that in those substances which exhibit polymorphism there is always one carbon atom, which is attached to four different radicles; by the change of orientation of this carbon atom, three different configurations of the same structural formula can be devised. It is, however, not improbable that the differences between the various modifications of the above substances are structural differences. Much may be said in favour of assigning the structurally different constitutions,  $\text{CPh}\cdot\text{C}(\text{OEt})\cdot\text{N}\cdot\text{OH}$  and  $\text{CPh}\cdot\text{C}(\text{OEt})\cdot\overset{\text{NH}}{\underset{\text{O}}{\text{C}}}$ , to the two ethylbenzhydroxamic acids, and the properties of the three ethylic paratolubenzhydroxamates seem to be satisfactorily explained by the following three formulæ,



W. J. P.

**Space Isomerism of Carbodiphenylimides and Carboditolylimides.** By C. SCHALL (*Ber.*, 1894, **27**, 2696—2700).—The author gives reasons for regarding the three modifications of each of these diimides as really isomeric, and not polymeric (compare Abstr., 1892, 1452; 1893, i, 701). The fourth ( $\delta$ ) modification of carbodiphenylimide, previously described, has been found to be a mixture of the  $\beta$ -diimide with triphenylguanidine.

C. F. B.

**Synthesis of Piperic acid and Piperine.** By A. LADENBURG and M. SCHOLTZ (*Ber.*, 1894, **27**, 2958—2960).—Piperonal does not condense with crotonaldehyde, but with acetaldehyde in presence of



alkali it yields *piperonalacraldehyde*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH:CH:CHO}$ , which crystallises in yellow plates, melts at  $70^\circ$ , boils at  $180\text{--}190^\circ$  (20 mm.), and has a slight aromatic odour. The *phenylhydrazone* forms yellow crystals, melts at  $160^\circ$ , and turns brown on exposure to light. The *anilide* crystallises in pale yellow needles melting at  $118^\circ$ . Piperic acid is formed by fusing piperonalacraldehyde with anhydrous sodium acetate and acetic anhydride; it is identical with the natural acid. The following salts were prepared from both acids, and were found to agree in properties:—The *potassium salt* crystallises in lustrous needles; the *sodium salt* is crystalline; the *calcium*, *barium*, and *magnesium salts* appear as if they were amorphous, but in reality consist of slender, microscopic needles; the *manganous salt* crystallises in lustrous, yellow plates, the *copper salt* in slender, blue, stellate needles. The *lead salt* is amorphous. J. B. T.

### Action of Methylic Iodide on Potassium Resacetophenone.

By G. GREGOR (*Monatsh.*, 1894, **15**, 437—445).—It has recently been shown by Wechsler (*Abstr.*, 1894, i, 521) that potassium resacetophenone is converted by the action of ethylic iodide into diethoxyacetophenone, both ethyl groups being present as ethoxy-groups. The author has continued the investigation, with the view of discovering whether any other compounds are formed in the action, and also to ascertain if analogous products could be obtained by the action of methylic iodide.

By the action of ethylic iodide on potassium resacetophenone, the author has obtained, in addition to the diethyl derivative, a *monomethyl*-derivative,  $\text{C}_8\text{H}_7\text{O}_2\text{:OEt}$ , which can be separated from the crude product by shaking the ethereal solution with potash. It crystallises in long, colourless needles, melts at  $48^\circ$ , and, with ferric chloride, gives a reddish-brown coloration with a tinge of violet.

The methylic derivatives are prepared by boiling a solution of resacetophenone and potash in methylic alcohol with methylic iodide, distilling off the alcohol, mixing with water, and extracting with ether. The ethereal solution is shaken with potash to remove phenolic compounds, and the oil which remains on evaporating the ethereal solution is dissolved in alcohol and precipitated with water. Two products are thus obtained, one separating in crystals and the other as an oil. The former is a mixture of a methyl- and dimethyl-resacetophenone, which may be separated by crystallisation from light petroleum, the monomethyl-derivative being present in small quantity only. The *dimethyl*-derivative is thus obtained in colourless plates; it melts at  $80\text{--}81^\circ$ , and only contains one methoxyl group; hence the compound has the constitution  $\text{C}_8\text{H}_6\text{O}_2\text{Me:OMe}$ . The substance which separates as an oil on adding water to the alcoholic solution has the composition of a dimethylresacetophenone, but the determination of the number of methoxyl groups shows that it is not homogeneous, but consists probably of a mixture of dimethoxyacetophenone with another dimethyl derivative.

The portion of the product which was soluble in alkali consists chiefly of the *monomethyl*-derivative, which, after crystallisation from alcohol, melts at  $49^\circ$ , and is coloured dark reddish-brown by ferric

chloride. It has the composition  $C_9H_{10}O_3$ , and contains one methoxyl group, and is therefore methoxy acetophenone,  $C_8H_7O_2 \cdot OMe$ .

H. G. C.

**Gallacetophenone.** By M. NENCKI (*Ber.*, 1894, **27**, 2737—2738).—The acetyl-group in gallacetophenone, chlorogallacetophenone, and gallobenzophenone has probably the same position as the carboxyl group in pyrogallolcarboxylic acid, namely is adjacent to an hydroxyl group. The three ketones named above all behave towards sulphuric acid in a similar manner to pyrogallolcarboxylic acid, a violet coloration being produced when sulphuric acid containing a trace of nitric acid is added to a dilute solution of the compound in sulphuric acid.

Chlorogalloacetophenone, moreover, is converted, by treatment with calcium carbonate, into the anhydroglycogallol,  $C_6H_2(OH)_3 \cdot CO \cdot CH_2Cl = C_6H_2(OH)_2 < \overset{O}{\underset{CO}{C}} > CH_2 + HCl$ . This behaviour is not shown by such compounds as chloracetocatechone,  $C_6H_3(OH)_2 \cdot CO \cdot CH_2Cl$  [ $OH : OH : COCH_2Cl = 1 : 2 : 4$ ], in which the chloracetyl group is not in the ortho-position to any of the hydroxyl-groups.

A. H.

**Interaction of the Sodium Derivatives of Phenol with Ethylic Monochloracetate and Dichloracetate.** By K. AUWERS and K. HAYMANN (*Ber.*, 1894, **27**, 2795—2806; compare Bischoff and Walden, *Abstr.*, 1894, i, 403).—*Ethylic diphenoxyacetate*,  $CH(OPh)_2 \cdot COOEt$ , prepared by heating phenol, ethylic dichloracetate, and sodium in alcoholic solution, is a pale yellow oil, which is readily hydrolysed by soda, and boils at  $208^\circ$  (28 mm.),  $229^\circ$  (41 mm.), or at  $240^\circ$  (53 mm.); the yield is 60 per cent. of the theoretical. The acid crystallises from glacial acetic acid in silky, lustrous needles, melts at  $91^\circ$ , and is less soluble in water than phenoxyacetic acid. The silver, lead, zinc, and copper salts are sparingly soluble; the sodium salt is crystalline. The amide crystallises in lustrous plates, melts at  $108^\circ$ , and in benzene solution gives abnormal cyroscopic results. The yield is almost quantitative. *Dibromodiphenoxyacetic acid*,  $CH(O \cdot C_6H_4Br)_2 \cdot COOH$ , formed by the action of aqueous bromine on the acid in glacial acetic acid solution, crystallises in slender needles melting at  $151^\circ$ . The silver and sodium salts are sparingly soluble; the former darkens on exposure to light. Diphenoxyacetic acid resembles phenoxyacetic acid in its behaviour towards nitric acid; it is scarcely attacked by dilute acid (sp. gr. 1.3), but with the concentrated acid yields nitrophenols.

*Ethylic di- $\alpha$ -naphthoxyacetate*,  $CH(O \cdot C_{10}H_7)_2 \cdot CO \cdot OEt$ , prepared in a similar manner to the phenoxy-derivative, is a viscid oil, and decomposes when distilled. The acid crystallises in lustrous prisms, and melts at  $174^\circ$ . The sodium salt crystallises in lustrous, concentric needles. *Ethylic di- $\beta$ -naphthoxyacetate* resembles the  $\alpha$ -derivative in properties and mode of preparation. The acid crystallises in prisms, and melts at  $134^\circ$ . The sodium salt is crystalline.

*Ethylic orthobromophenoxyacetate*,  $C_6H_4Br \cdot O \cdot CH_2 \cdot COOEt$ , prepared from orthobromophenol, ethylic chloracetate, and sodium ethoxide, boils at  $160$ — $170^\circ$  (16 mm.). The acid crystallises in pearly, lustrous plates, melts at  $142.5$ — $143^\circ$ , and decomposes when distilled.

Attempts to eliminate hydrogen bromide by the action of alkalis, under varied conditions, were unsuccessful. The *amide* crystallises in colourless plates, melts at  $151^{\circ}$ , and boils at  $250\text{--}300^{\circ}$  under the ordinary pressure.

Methylic salicylate and ethylic chloracetate combine, forming an oily, ethereal salt, which, on hydrolysis, yields salicyloacetic acid,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$ ; this crystallises from benzene in needles, from water in pearly, lustrous plates, and melts at  $191\cdot5\text{--}192^{\circ}$ , not at  $186\text{--}187^{\circ}$  as stated by Rössing, who prepared it by the oxidation of orthaldehydophenoxyacetic acid.

Guaiacol readily combines with ethylic chloracetate and ethylic dichloracetate; *ethylic guaiacolglycollate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOEt}$ , formed in the latter case, is a colourless, oily liquid boiling at  $175\text{--}179^{\circ}$  (27 mm.). The acid has recently been described by Cutolo (Abstr., 1894, i, 289); the *amide* is deposited from benzene in colourless, lustrous, concentric crystals melting at  $138^{\circ}$ .

Dibromonitrophenol [ $\text{OH} : \text{Br} : \text{NO}_2 : \text{Br} = 1 : 2 : 4 : 6$ ], ortho- and para-nitrophenols, and ortho- and para-hydroxybenzoic acids, do not react with ethylic chloracetate; resorcinol has little action on ethylic dichloracetate, and ortho- and para-nitrophenol none; thiophenol and ethylic dichloracetate yield phenylic bisulphide.

The authors have postponed the full investigation of their subject until the completion of Bischoff and Walden's work (*loc. cit.*). The above results show the great influence exerted by a second negative group in the benzene nucleus; its position and nature, whether nitro-, carboxyl-, or hydroxyl-, are of little importance, and the presence of a halogen atom in the benzene ring does not appear to affect the reaction.

J. B. T.

**Constitution of Phloretin.** By Mrs. H. A. MICHAEL (*Ber.*, 1894, 27, 2686—2689).—When phloretin is treated with acetic anhydride in the presence of a little zinc chloride, anhydrous sodium acetate, or stannic chloride, it yields a *triacetyl*-derivative melting at  $93\cdot5\text{--}94\cdot5^{\circ}$ , not a diacetyl derivative as Schiff (*Annalen*, 156, 1) thought. If the mixture is heated for 2—3 hours, a substance melting at  $166\text{--}167^{\circ}$  is formed, probably a condensation product of phloretin. Phloretin itself is probably the phloroglucinol salt of phloretic acid, with the formula  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_4\cdot\text{COO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ .

C. F. B.

**Ethylic Isophthalodicyanacetate.** By J. LOCHER (*Compt. rend.*, 1894, 119, 274—276).—*Ethylic isophthalodicyanacetate* is obtained in the same way as the terephthalic derivative (Abstr., 1894, i, 593) by the action of isophthalic chloride on ethylic sodiocyanacetate in presence of ether. It forms white microscopic needles which melt at  $191\text{--}192^{\circ}$ ; it is insoluble in water, but very soluble in chloroform, and also dissolves in other organic solvents. Boiling water, alkalis, and strong acids decompose it with formation of isophthalic acid and ethylic cyanacetate.

Ethylic isophthalodicyanacetate acts as a bibasic acid, and can be titrated in dilute alcoholic solution with phenolphthaleïn as indicator. The disilver derivative is a white amorphous powder which is insoluble in water and becomes black when exposed to light; the cupric deriva-

tive forms green crystals containing  $2\text{H}_2\text{O}$ , which is given off in a vacuum; the ferric derivative is a brownish red crystalline powder insoluble in water and organic solvents; the ammonium salt is a white crystalline powder which dissolves in water, and melts and decomposes at  $130\text{--}133^\circ$ .

The dimethyl-derivative,  $\text{C}_6\text{H}_4[\text{CO}\cdot\text{CMe}(\text{CN})\cdot\text{COOEt}]_2$ , is easily obtained by the action of methylic iodide on the silver derivative in presence of methylic alcohol. It crystallises from methylic alcohol in brilliant white microscopic needles which melt at  $188^\circ$ , and are insoluble in water and solutions of alkalis, but dissolve in organic solvents.

The dihydrazone is readily obtained in the same way as the para-derivative, and crystallises from alcohol in white microscopic needles which melt at  $260\text{--}261^\circ$ , and become red on exposure to air. It is very slightly soluble in all organic solvents, and is insoluble in water, but is decomposed by hot water, alkalis, and acids.

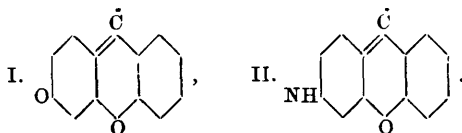
The author has been unable to obtain the meta- and para-derivatives corresponding to the orthophthalomonocyanacetate described by Muller.

C. H. B.

**Action of Aniline Bases on Benzoïn.** By B. LACHOWICZ (*Monatsh.*, 1894, **15**, 402—403).—A recent publication by Japp and Murray (*Abstr.*, 1894, i, 90) has led the author to revise his previous work (*ibid.*, 39). He now finds that  $\alpha\beta$ -diphenylanilindole, which melts at  $125^\circ$ , results from the interaction of aniline hydrochloride and benzoïn anilide, whilst paratoluidine hydrochloride and benzoïn anilide give rise to the same product, and, in addition to  $\alpha\beta$ -diphenylparatoluidole, which melts at  $155^\circ$ . The last-named product also results from the interaction of paratoluidine hydrochloride and benzoïn-paratoluidide, whilst aniline hydrochloride and benzoïnparatoluidole yield both the indoles, and these can be separated by repeated recrystallisation.

G. T. M.

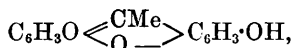
**Fluoresceïn Colouring Matters.** By R. MÖHLAU and P. KOCH (*Ber.*, 1894, **27**, 2887—2897).—The author applies the name of *fluorone* to substances containing the group I, and of *fluorime* to the corresponding imides, II; the name of the acid or aldehyde from which the central CR group in each compound is supposed to be derived being prefixed.



*Formaldehydhydroxyfluorone*,  $\text{C}_6\text{H}_3\text{O}\langle\text{CH}\rangle\text{C}_6\text{H}_3\text{OH}$ , is formed when diresorcinylmethane (*Abstr.*, 1892, 856) is warmed with concentrated sulphuric acid, or zinc chloride and a little aluminium chloride, but has not been obtained quite pure. It is readily soluble in alkalis, the dilute solutions having an intense green fluorescence. The *diorescinylmethane* ("methylenediorescinol"),  $\text{CH}_2[\text{C}_6\text{H}_2\text{Me}(\text{OH})_2]_2$ ,

was obtained by the action of formaldehyde on orcinol in the presence of sulphuric acid. It forms small white crystals, is insoluble in water, and, when heated, decomposes without melting. *Formaldehydhydroxytolufluorone*,  $C_6H_3MeO \llcorner \begin{smallmatrix} CH \\ O \end{smallmatrix} \_ > C_6H_3Me \cdot OH$ , prepared from diorcinylmethane, separates from methylic alcohol in dark-brown, crystalline granules. Its solutions in alkalis have a yellowish-green fluorescence.

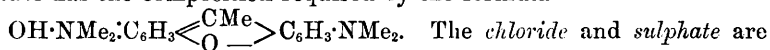
The product of the condensation of acetaldehyde with resorcinol appears to be a mixture of two different substances, formed by the interaction of the two in different proportions, but may be used for the preparation of *acetaldehydhydroxyfluorone*,



which is a yellowish-brown substance resembling the formaldehyde-compound in properties.

Acetaldehyde also reacts with orcinol, but it has not been found possible to obtain the condensation product or the corresponding fluorone in the pure state.

Dimethylmetamidophenol reacts with acetaldehyde in the presence of hydrochloric acid to form *ethylidenetetramethylmetamidophenol*  $CMe[C_6H_3(OH) \cdot NMe_2]_2$ , which is a light-violet coloured crystalline substance, melts at  $140^\circ$ , and is soluble in acids and alkalis. When this substance is heated with sulphuric acid, *tetramethyldiamidodiphenylethylidene oxide* is formed and may be precipitated by caustic soda as a violet coloured mass. On oxidation with ferric chloride or sodium nitrite in presence of hydrochloric acid, a salt of *acetaldehydetetramethylamidofluorimum hydrochloride* is formed and may be salted out in the usual way; zinc chloride precipitates the zinc double salt. Alkalis added to the solution of the colouring matter precipitate the *colour base*, which is a dark violet, crystalline mass, melting at  $152^\circ$ . Its solutions in dilute acids are red, and show a strong yellow fluorescence. When dried over sulphuric acid, the base has the composition required by the formula



The *chloride* and *sulphate* are very soluble, the *picrate* and *iodide* sparingly soluble. The *platinochloride* forms dark plates with green metallic lustre. Formaldehyde condenses with dimethylamidophenol in a similar manner, producing *tetramethyldiamidodihydroxydiphenylmethane*, which crystallises in small violet plates melting at  $175^\circ$ . When treated with dehydrating and oxidising agents it yields *formaldehydetetramethylamidofluorimum chloride*, the zinc double salt of which is known commercially as pyronine (German patent, No. 59003).

A. H.

**Compounds containing the Group  $C_nH_2O_2$ .** By A. ANGELI (*Gazzetta*, 1894, **24**, ii, 59—67; compare *Abstr.*, 1893, i, 355).—The author discusses the constitutions of compounds containing the group  $C_nH_2O_2$  and their derivatives, which he has investigated.

W. J. P.

**1 : 5-Diketones.** By E. KNOEVENAGEL (*Annalen*, 1894, **281**, 25—126; compare *Abstr.*, 1893, i, 419 and 697).—Symmetrical derivatives of this type are obtained by the condensation of aldehydes with ethylic acetoacetate and analogous compounds under the influence of primary and secondary amines (Hantzsch), whilst unsymmetrical 1 : 5-diketones are prepared by the addition of substances containing salt-forming methylenic hydrogen to unsaturated compounds, in the presence of sodium ethoxide or primary and secondary amines. The formation of pyridine derivatives by the action of hydroxylamine on 1 : 5-diketones is limited to those which do not undergo the intramolecular condensation already described (*loc. cit.*).

*Ketophenylparacophenone*,  $\text{O} \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \text{CHPh} \end{smallmatrix} \text{CH} \cdot \text{COPh}$  (compare W.

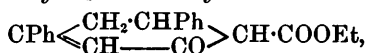
Wislicenus, *Abstr.*, 1893, i, 714), is obtained by saturating a well-cooled mixture of ethylic benzoylpyruvate and benzaldehyde with hydrogen chloride. When warmed with strong potash, a solution exhibiting yellow fluorescence is produced, and benzaldehyde is eliminated. It melts at  $212^\circ$ , and prolonged exposure to the temperature  $220$ — $230^\circ$  causes it to become deep red, equal volumes of carbonic oxide and anhydride being evolved; the residual oil yields benzylideneacetophenone when distilled in a vacuum. Brought in contact with deoxybenzoin in presence of sodium ethoxide, ketophenylparacophenone gives rise to *deoxybenzoinbenzylideneacetophenone*,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{COPh}$ , which melts at  $189^\circ$ ; it is also formed by mixing together the alcoholic solutions of benzylideneacetophenone and deoxybenzoin with sodium ethoxide. On heating it with hydroxylamine hydrochloride (2—3 mols.) in dilute alcoholic solution for four hours at  $140$ — $150^\circ$ , 2 : 4 : 5 : 6-tetraphenylpyridine is formed, which crystallises in colourless needles melting at  $179^\circ$ , whilst the *oxime* of deoxybenzoinbenzylideneacetophenone is produced when the constituents are heated together for two hours on the water bath; this melts at  $212^\circ$ , and yields 2 : 4 : 5 : 6-tetraphenylpyridine under the influence of hydrogen chloride.

*Ethylic benzylidenedibenzoylpyruvate*,  $\text{CHPh}(\text{CHBz} \cdot \text{CO} \cdot \text{COOEt})_2$ , is prepared by adding a few drops of diethylamine or piperidine to a mixture of benzaldehyde and ethylic benzoylpyruvate (2 mols.); it melts at  $162^\circ$ . When boiled with water, one molecular proportion of ethylic benzoylpyruvate is eliminated, with formation of ketophenylparacophenone.

Ethylic benzylidenedibenzoylacetate (Buchner and Curtius, *Abstr.*, 1885, 1238) is produced by the condensation of ethylic benzoylacetate with benzaldehyde under the influence of diethylamine; it melts at  $95^\circ$ . *Ethylic 2 : 4 : 6-triphenylpyridine-3 : 5-dicarboxylate*, which melts at  $146^\circ$ , is obtained from it by heating with hydroxylamine for four hours at  $120$ — $130^\circ$ .

*Ethylic methylenedibenzoylacetate*,  $\text{CH}_2(\text{CHBz} \cdot \text{COOEt})_2$ , melting at  $86^\circ$ , is prepared by adding a few drops of diethylamine to a mixture of ethylic benzoylacetate and formaldehyde solution.

*Ethylic 3 : 5-diphenyl- $\Delta_2$ -ketotetrahydrobenzene-6-carboxylate*,



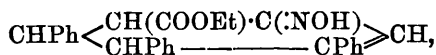
is obtained by the interaction of ethylic acetoacetate and benzylidenacetophenone in presence of sodium ethoxide; it melts at 109°. When heated with dilute hydrochloric acid for four hours at 160°, it yields 3 : 5-diphenyl- $\Delta_2$ -ketotetrahydrobenzene, which melts at 70—72°.

*Deoxybenzoïnparacinnamylanisoil* (deoxybenzoïnbenzylideneparamethoxyacetophenone),  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{COPh}$ , is obtained by adding alcoholic potash to a mixture of cinnamylanisoil and deoxybenzoïn in molecular proportion; it melts at 206°. Substituting ethylic malonate for deoxybenzoïn, the compound  $\text{C}_{19}\text{H}_{18}\text{O}_6$  is formed, melting at 166°, whilst benzylic cyanide gives rise to the compound  $\text{C}_{24}\text{H}_{22}\text{O}_4$  when heated with cinnamylanisoil and hydrochloric acid for two hours at 120°; this melts at 201°.

*Ethylic deoxybenzoïnbenzylideneacetoacetate*,

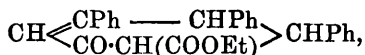


is obtained by adding sodium ethoxide to a mixture of ethylic benzylideneacetoacetate and deoxybenzoïn in molecular proportion dissolved in alcohol; it melts at 123°. The action of hydroxylamine on this substance gives rise to an *oxime* of the constitution



in place of a pyridine derivative, two molecules of water having been eliminated instead of three. This oxime melts and decomposes at 150—155°.

*Ethylic 3 : 4 : 5-triphenyl- $\Delta_2$ -ketotetrahydrobenzene-6-carboxylate*,



is prepared by passing hydrogen chloride through alcohol in which ethylic deoxybenzoïnbenzylideneacetoacetate is suspended; it melts at 184°. When boiled for several hours with alcoholic potash (rather more than 2 mols.), it is converted into iso-3 : 4 : 5-triphenyl- $\Delta_2$ -ketotetrahydrobenzene, which melts at 138°; this is also formed on boiling a mixture of ethylic benzylideneacetoacetate and deoxybenzoïn (1 mol.) with caustic potash (rather less than 2 mols.); if the proportion of potash used is greater than this, or if the foregoing compound is heated in alcoholic solution with a few drops of potash, 3 : 4 : 5-triphenyl- $\Delta_2$ -ketotetrahydrobenzene, melting at 186°, is produced (compare Abstr., 1893, i, 419); the *oxime* melts at 209°, whilst its *isomeride* melts at 120°.

Triphenylbenzene,  $[\text{Ph}_3 = 1 : 2 : 3]$ , is formed when 3 : 4 : 5-triphenyl- $\Delta_2$ -ketotetrahydrobenzene or its *isomeride* is distilled with zinc chloride; it melts at 150—155° (compare A. Smith, Abstr., 1893, i, 220). Triphenylketotetrahydrobenzene yields a *bromo-derivative*, which melts at 218°, the *isomeride* melting at 175°. Potassium permanganate has no action on triphenylketotetrahydrobenzene, but is at once decolorised when the isomeric modification is warmed with it.

Condensation of ethylic benzylideneacetoacetate with deoxybenzoïn

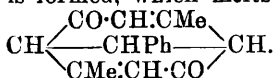
and ammonia gives rise to *ethylic methyltriphenyldihydropyridinecarboxylate*,  $\text{CPh} \begin{smallmatrix} \text{CPh} \cdot \text{CHPh} \\ \text{NH} - \text{CMe} \end{smallmatrix} \text{C} \cdot \text{COOEt}$  (compare Paal and Strasser, Abstr., 1888, 62); it melts at  $170^\circ$ .

Ethylic 3-methyl-5-phenyl- $\Delta_2$ -ketotetrahydrobenzene-4 : 6-dicarboxylate (Abstr., 1893, i, 419) yields an *oxime*, which melts at  $173^\circ$ .

*Benzylideneacetylacetone*,  $\text{CAc}_2 \cdot \text{CHPh}$ , which boils at  $185-188^\circ$  (15 mm.), is obtained by heating the *hydrochloride* above its melting point in a vacuum, this salt being formed on leading hydrogen chloride into a well-cooled mixture of acetylacetone and benzaldehyde (1 mol.); it melts at  $104-105^\circ$ , hydrogen chloride being eliminated. *Benzylidenediacetylacetone*,  $\text{CHPh}(\text{CHAc}_2)_2$ , is produced when a few drops of diethylamine are added to a mixture of acetylacetone with benzylideneacetylacetone in molecular proportion, or by the influence of the same base on a mixture of benzaldehyde with acetylacetone (2 mols.); it melts at  $166^\circ$ . Hydroxylamine gives rise to a *compound* which melts at  $145^\circ$ , and phenylhydrazine yields a *compound* of the formula  $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_2$ , melting at  $177^\circ$ .

3-Methyl-5-phenyl- $\Delta_2$ -ketotetrahydrobenzene,  $\text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{CH}_2 \\ \text{CO} - \text{CH}_2 \end{smallmatrix} \text{CHPh}$ , is formed on boiling benzylidenediacetylacetone with caustic potash; it melts at  $35-36^\circ$ , and boils at  $189-194^\circ$  (15-20 mm.). It is also formed when ethylic 3-methyl-5-phenyl- $\Delta_2$ -ketotetrahydrobenzene-4 : 6-dicarboxylate is boiled with caustic potash or heated with dilute hydrochloric acid at  $160^\circ$ . A more convenient method of preparation consists in boiling ethylic benzylidenediacetoacetate with a 10 per cent. solution of caustic potash. The *oxime* melts at  $115^\circ$ .

Ethylic benzylideneacetylacetoneacetoacetate is formed when a few drops of diethylamine are added to a mixture of benzylideneacetylacetone and ethylic acetoacetate (1 mol.); it melts at  $156^\circ$ , and is converted into the foregoing compound when boiled with dilute caustic potash. When hydrogen chloride is led through absolute alcohol in which benzylidenediacetylacetone is suspended, a *compound* is formed, which melts at  $152^\circ$ , and probably has the constitution



Deoxybenzoinbenzylideneacetylacetone,  $\text{CHAc}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{COPh}$ , is produced by the addition of a few drops of diethylamine to a mixture of benzylideneacetylacetone and deoxybenzoin (1 mol.) in alcohol; it melts at  $191-192^\circ$ . The *oxime* melts at  $205-206^\circ$ . 3 : 4 : 5-Triphenyl-6-acetyl- $\Delta_2$ -ketotetrahydrobenzene,

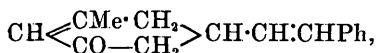


melting at  $221^\circ$ , is formed by the action of rather less than one molecular proportion of sodium ethoxide on the foregoing ketone; the employment of two leads to the formation of 3 : 4 : 5-triphenyl- $\Delta_2$ -ketotetrahydrobenzene.

Ethylic cinnamylidenediacetoacetate,  $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{CHAc} \cdot \text{COOEt})_2$ , is obtained by the condensation of cinnamaldehyde with ethylic



acetoacetate (2 mols.) under the influence of diethylamine or piperidine (compare Biginelli, Abstr., 1890, 768). It melts at 160—161°, and if submitted to the action of hydrogen chloride, when suspended in well-cooled absolute alcohol, it gives rise to *ethylic 3-methyl-5-cinnamyl-Δ<sub>2</sub>-ketotetrahydrobenzene-4:6-dicarboxylate*, which melts at 127°. Employing warm caustic soda instead of hydrogen chloride, *3-methyl-5-cinnamyl-Δ<sub>2</sub>-ketotetrahydrobenzene*,



is obtained. It melts at 56° and boils at 243° (10 mm.); the *oxime* melts at 176—177°.

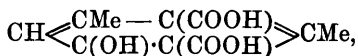
Ethylic methylenediacetoacetate (ethylic diacetylglutarate) is prepared by adding a small quantity of diethylamine or piperidine dissolved in alcohol to a mixture of 40 per cent. formaldehyde solution with ethylic acetoacetate (2 mols.), the liquid being well cooled for 5—6 hours. It forms a viscid oil, free from colour and odour; it boils and decomposes at 190—210° (20 mm.). Ammonia converts it into ethylic dihydrolutidinedicarboxylate (compare Griess and Harrow, Abstr., 1888, 1313). Water is eliminated from ethylic methylenediacetoacetate with formation of ethylic 3-methyl-Δ<sub>2</sub>-ketotetrahydrobenzene-4:6-dicarboxylate, the latter substance yielding 3-methyl-Δ<sub>2</sub>-ketohexenylene on hydrolysis (compare Hagemann, Abstr., 1893, i, 394). The *oxime* melts at 63°, and its *hydrochloride* at 159°; the *benzoyl*-derivative of the *oxime* forms lustrous needles which melt at 116°.

*Tetrahydrometatoluidine*,  $\text{CH} \begin{array}{c} \text{CMe} - \text{CH}_2 \\ \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \end{array} > \text{CH}_3$ , is obtained by heating 3-methyl-Δ<sub>2</sub>-ketotetrahydrobenzene with ammonium formate for five hours at 220—230°, and subsequent hydrolysis of the *formyl*-derivative, which boils at 260—275°. The free base forms a colourless liquid having an odour suggestive both of camphor and of ammonia; it boils at 152—155°, and is very volatile in a current of steam. The *hydrochloride* is readily soluble in water and alcohol, the aqueous solution decomposing when heated; the *platinochloride* melts and decomposes at 280°. The *carbamido*-derivative forms large, transparent plates which melt at 176°, and the *phenylthiocarbamido*-derivative crystallises from dilute alcohol in slender, lustrous needles which melt at 122°.

*Ethylic ethylidenediacetoacetate*,  $\text{CHMe}(\text{CHAc} \cdot \text{COOEt})_2$ , is prepared like ethylic methylenediacetoacetate, acetaldehyde being substituted for formaldehyde; it melts at 79—80°. Ammonia converts it into ethylic dihydrocollidinedicarboxylate, whilst by the action of phenylhydrazine the *phenylhydrazide* of ethylic 3:5-dimethyl-6-carboxylic-Δ<sub>2</sub>-ketotetrahydrobenzene-4-carboxylate is obtained; this is also formed by the interaction of ethylic methylenediacetoacetate and phenylhydrazine.

*Ethylic 3:5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene-4:6-dicarboxylate*,  $\text{CH} \begin{array}{c} \text{CMe} \cdot \text{CH}(\text{COOEt}) \\ \text{CO} \cdot \text{CH}(\text{COOEt}) \end{array} > \text{CHMe}$ , is obtained by the elimination of 1 mol. H<sub>2</sub>O from ethylic ethylidenediacetoacetate under the influence

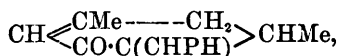
of heat or dilute acids and alkalis; it is a colourless oil which boils and decomposes at 225—230° (35 mm.). The *oxime*, which melts at 175°, is obtained by the action of hydroxylamine on ethylic ethylidenediaceoacetate. Bromine gives rise to the  *dibromide* , a viscid, colourless oil from which 2HBr is eliminated at 120°, yielding a  *compound*  which melts at 148° and boils at 258° (30 mm.); this, on hydrolysis, yields  *dimethylhydroxyisophthalic acid* ,



in minute, colourless needles, which melt and decompose at 228°, carbonic anhydride being eliminated and 1 : 3 : 5-xenol formed.

*Ethylic 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene-4-carboxylate* is produced, together with  *ethylic 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene-6-carboxylate* , by the hydrolysis of ethylic 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene-4 : 6-dicarboxylate; the ethylic β-carboxylate is separated from the δ-isomeride by its solubility in caustic soda.

Hydrolysis of ethylic ethylidenediaceoacetate gives rise to 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene, which yields the  *oxime*  melting at 166—168°, in addition to the compound described by Hantzsch (Abstr., 1883, 84), which melts at 72—74° and boils at 140—141° (19 mm.), whilst the  *hydrochloride*  melts at 169—170°, and the  *benzoyl-derivative*  at 126°. The  *phenylhydrazone*  of 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene melts at 76—78° and boils at 210—215° (20 mm.), whilst the  *benzylidene-derivative* , having the constitution



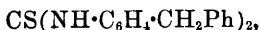
melts at 102°; the latter is identical with the benzylidene-derivative described by Sarelli (Abstr., 1893, i, 667).

The  *dibromide*  of 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene is a colourless, unstable oil, which is readily converted into Hantzsch's tetrabromo-derivative melting at 136°; a  *bromide*  melting at 86° is formed when the ketone is exposed to sunlight for 36 hours in contact with a large excess of bromine.

*Tetrahydro-xylidine*,  $\text{CH} \begin{array}{c} \text{CMe} - \text{CH}_2 \\ \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \end{array} \text{CHMe}$ , is obtained by reducing the  *oxime*  of 3 : 5-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene, in alcoholic solution, with sodium, or by heating the ketone with ammonium formate for five hours at 230—240°; it boils at 169—170°, and is volatile with ether vapour. The  *hydrochloride*  melts at 140—150°; the  *platinochloride*  crystallises in lustrous, orange-coloured plates, which melt and decompose at 260°; the  *formyl-derivative*  boils at 156—158° (18 mm.). The  *carbamido-derivative*  melts at 185°, and the  *phenylthiocarbamido-derivative*  forms long, lustrous needles, which melt at 172°. M. O. F.

**Orthamidodiphenylmethane.** By O. FISCHER and H. SCHMIDT (Ber., 1894, 27, 2786—2790).—The preparation of orthamidodiphenylmethane has been previously described (Abstr., 1894, i, 200). The  *sulphate* , (C<sub>13</sub>H<sub>13</sub>N)<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub>, crystallises in colourless needles, and

melts at 191°. The *benzoyl*-derivative crystallises in long, colourless, lustrous prisms melting at 116°. The *thiocarbamide*,



is deposited in small, pale yellow crystals, and melts at 147°.

*Phthalylamidodiphenylmethane*,  $\text{C}_6\text{H}_4\cdot\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$ , formed from phthalic anhydride and the amine, crystallises in colourless needles, and melts at 139°. *Parahydroxybenzylidenamidodiphenylmethane* and *paranitrobenzylidenamidodiphenylmethane* are formed by the interaction of the amine and parahydroxybenzaldehyde and paranitrobenzaldehyde respectively; the former is deposited in small, yellow plates melting at 110°, the latter in golden crystals melting at 105°. *Orthohydroxydiphenylmethane* and fluorene are converted into the amine by the diazo-reaction; the former is an oily liquid, volatile with steam, soluble in soda, and yielding xanthine, in small quantity, by distillation with lead oxide.

*Diphenylmethaneorthazo-β-naphthol*, prepared from the diazo-chloride and β-naphthol, crystallises in red needles, and melts at 134°. Two dyes are formed by the interaction of the diazo-chloride and resorcinol, they crystallise in reddish-brown needles, and can be separated by means of alcohol. The more soluble is *diphenylmethaneorthazodihydroxybenzene*, melting at 170°; the other melts at 189°. The *sodium salts* of both are sparingly soluble.

*Orthocyanodiphenylmethane*, prepared from the diazo-chloride and potassium cyanide, is a pale yellow oil with a characteristic odour; it boils at 300—305° (147 mm.), and by prolonged heating with alcoholic potash is converted into *benzylbenzamide*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises in colourless needles, melts at 162°, and, when boiled during several days with alcoholic soda, yields benzylbenzoic acid. Anthranol is produced by the action of concentrated sulphuric acid (20 parts) at 90° on benzylbenzoic acid; its formation is probably preceded by that of anthraquinone.

J. B. T.

**The Benzene Nucleus.** By W. VAUBEL (*J. pr. Chem.*, 1894, [2], 50, 362—366).—Auramine, amidotetramethyldiamidodiphenylmethane, reacts with four atoms of nascent bromine, instead of the two, required by the author's theory. This is probably due to the presence of the amido-group combined with the methane carbon atom. Similar behaviour is shown by other compounds. Tetramethyldiamidobenzophenone reacts with the normal number of bromine atoms, whilst the corresponding benzhydrol, in which a hydroxy-group is combined with the methane carbon atom, resembles auramine and reacts with four.

The author also replies to Knorr's criticisms (*Annalen*, 1894, 279, 188) on his views as to the configuration of the benzene molecule, and endeavours to show, by arguments which cannot be rendered intelligible without models, that the behaviour of the phthalic acids, the constitution of pyrazole, and the etherification of aromatic acids can all be readily explained on the principles already laid down by him (*Abstr.*, 1891, 1343).

A. H.

**Paradiamidodiphenylmethanesulphone.** By O. STEIN (*Ber.*, 1894, **27**, 2806—2807; compare Eberhardt and Welter, *Abstr.*, 1894, i, 451).—*Paradiamidodiphenylmethanesulphone* is the chief product of the action of fuming sulphuric acid on paradiamidodiphenylmethane, under the conditions described by the author. It crystallises from dilute ammonia in colourless, lustrous plates, melts at 217°, and becomes yellow by the prolonged action of ammonia. It gives an intense blue coloration with extremely small traces of nitrous acid, but the colour soon changes to reddish-brown, and may completely disappear after a time. No coloration is produced with diazo-compounds, and the sulphone might, therefore, be employed as an indicator in the titration of aromatic amines with sodium nitrite.

J. B. T.

**Tetrahydrocarbazole.** By C. U. ZANETTI and E. LEVI (*Gazzetta*, 1894, **24**, ii, 111—118).—On heating tetrahydrocarbazole with methylic iodide at 120—140° in an autoclave, and distilling the product in a current of steam, an oil is obtained, which partially dissolves in hydrochloric acid; the residue ultimately solidifies, and is found to be a mixture melting at 152—165°. If the hydrochloric acid solution, after treatment with sodium nitrite, is extracted with ether, and the ethereal solution evaporated, a *nitrosamine* is left; this, on reduction, yields a secondary base. The principal product of the action remains dissolved in the original hydrochloric acid solution, and is a

base of the composition  $C_{14}H_{17}N$ , possibly  $\begin{array}{c} CH:CH \cdot C \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \\ | \qquad \qquad | \\ CH:CH \cdot C \cdot NMe \cdot C \cdot CH_2 \cdot CH_2 \end{array}$

It is a heavy, yellow oil, which boils at 160—165° under 14 mm. pressure, has an aromatic odour, and decomposes slowly in the air. The platinochloride,  $(C_{14}H_{17}N_2)_2, H_2PtCl_6$ , crystallises in lustrous, brick-red needles melting and decomposing at 204—208°.

On gradually adding chloroform to an alcoholic solution of tetrahydrocarbazole and sodium ethoxide, a *base*,  $C_{13}H_{13}Cl_2N$ , probably  $\begin{array}{c} CH:CH \cdot C \cdot CCl_2 \cdot C \cdot CH_2 \cdot CH_2 \\ | \qquad \qquad | \\ CH:CH \cdot C \cdot NH \cdot C \cdot CH_2 \cdot CH_2 \end{array}$ , is formed, which may be separated from the product by decomposing its hydrochloride with alkali and extracting with ether. The base crystallises in thin, white laminae melting at 158—159°, and has feebly basic properties; the *platinochloride* is very unstable. On heating the base with hydriodic acid and red phosphorus at 220—230°, it yields a product containing chlorine, and possessing the powerful odour of an isonitrile.

W. J. P.

**Phenolphthalein anhydrideanilide and Gallein anilide.** By R. ALBERT (*Ber.*, 1894, **27**, 2793—2794; compare *Abstr.*, 1894, i, 201).—*Phenolphthalein anhydride*, prepared by fusing a mixture of phenol, phthalic anhydride, and zinc chloride, is insoluble in alkalis, and readily forms an *anilide*,  $CO < \begin{smallmatrix} C_6H_4 \\ NPh \end{smallmatrix} > C < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > O$ , which crystallises in short, colourless, lustrous prisms.

*Gallein anilide*,  $CO < \begin{smallmatrix} C_6H_4 \\ NPh \end{smallmatrix} > C < \begin{smallmatrix} C_6H_2O(OH) \\ C_6H_2O(OH) \end{smallmatrix} > O$ , formed by heating gallein with aniline (6 parts) and aniline hydrochloride (2 parts),

crystallises from alcohol or glacial acetic acid in colourless, lustrous plates, and melts above  $300^{\circ}$ . The *dimethylic ether* crystallises in slender, colourless needles, and melts at  $205^{\circ}$ . J. B. T.

**Fluoresceïn-anilides.** By O. FISCHER and F. HEPP (*Ber.*, 1894, 27, 2790—2793; compare *Abstr.*, 1893, i, 721, and preceding abstract).—The phthaleïns are divisible into three groups. The term *leucophthaleïns* is applied to those which, together with their simpler derivatives, are colourless, and are probably represented by Baeyer's phthaleïn formula. The coloured phthaleïns, which also yield coloured salts, ethers, and simple substitution products, are termed *quinoidal phthaleïns*; fluoresceïn and galleïn belong to this class. *Tautophthaleïns* are those which are colourless but yield coloured salts, such as phenolphthaleïn, paradiamidophthalophenone, and orcinolphthaleïn.

Fluoresceïn-anilide dimethylic ether is not hydrolysed by boiling with dilute alcoholic sulphuric acid, but is by the action of hydrochloric acid at  $150^{\circ}$ ; *fluoresceïn dimethylic ether* is formed, and crystallises in slender, colourless needles, melting at  $198^{\circ}$ . It gives a red coloration, in alcoholic solution, with mineral acids, and dissolves in concentrated sulphuric acid with a green fluorescence. *Fluoresceïn-anilide diethylic ether* crystallises in colourless prisms, melts at  $162$ — $164^{\circ}$ , loses alcohol of crystallisation by prolonged boiling at  $120^{\circ}$ , and gives a green fluorescence with concentrated sulphuric acid. By the prolonged action of concentrated acids, fluoresceïn-anilide diethylic ether is hydrolysed, aniline, alcohol, fluoresceïn, and *isofluoresceïn diethylic ether*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OEt}) \\ \text{C}_6\text{H}_3(\text{OEt}) \end{smallmatrix} > \text{O}$ , being formed; the last, after repeated crystallisation from benzene and ether, is deposited in colourless, tetragonal prisms, becomes yellow, and melts at  $181$ — $182^{\circ}$ . With sulphuric acid, it gives a yellow solution with green fluorescence. In alcoholic solution, mineral acids give a red coloration. Baeyer's fluoresceïn diethylic ether is yellow, and is probably the quinoidal form. Attempts to prepare colourless fluoresceïn from either of the ethers were unsuccessful.

*Phthalophenoneanilide*,  $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{NPh} \end{smallmatrix} > \text{CPh}_2$ , prepared from phthalophenone, aniline, and aniline hydrochloride, crystallises in vitreous prisms, melts at  $189^{\circ}$ , dissolves without coloration in concentrated sulphuric acid, and is precipitated on dilution. It is resolved into its constituents by the action of concentrated hydrochloric acid at  $180^{\circ}$ , but with alcoholic sulphuric acid (30 per cent.), at the same temperature, the larger part remains unchanged even after eight hours' heating. J. B. T.

**Action of Nascent Bromine on the Triphenylmethane Colouring Matters.** By W. VAUBEL (*J. pr. Chem.*, 1894, [2], 50, 347—351; compare *Abstr.*, 1893, i, 360).—Nascent bromine acts on the amido-triphenylmethane colouring matters in accordance with the rules already established by the author, that the amido- and monalkyl-amido-groups favour the introduction of bromine into the para- and the two ortho-positions, whilst the dialkylamido-group only permits its entrance into the para- and one ortho-position. This must, how-

ever, be slightly modified when applied to these dyes, since the characteristic mode of combination of one of the nitrogen atoms in some instances seems to affect the number of atoms of bromine which can be taken up.

The action, in most cases, proceeds quantitatively, and may be employed for the determination of the amount of colouring matter present. Tetramethyldiamidotriphenylmethane, "brilliant-green," and "methyl-green" react with two atoms of bromine; hexamethylparaleucaniline and "crystal-violet" require three atoms, rosaniline four, and leucaniline and pararosaniline five atoms. Aurin and phenolphthalein both require four atoms of bromine, this being in accordance with the previous conclusions drawn by the author from his former experiments on hydroxy-compounds.

A. H.

**The Triphenylmethane Colouring Matters.** By W. VAUBEL (*J. pr. Chem.*, 1894, [2], 50, 351—361; compare preceding abstract).—The fact that leucaniline reacts with five atoms of nascent bromine, whilst rosaniline only reacts with four, shows that the number of atoms of bromine taken up by the molecule is influenced by the mode of combination of one of the nitrogen atoms in rosaniline, and the author considers that only the formula of E. and O. Fischer can explain this phenomenon. He further shows that if the total number of atoms of bromine which can be introduced into the molecule of a colouring matter by treating it with nascent bromine, be taken as a measure of the total basicity of the amido-groups of the compound, it will be found that as the basicity increases the colour of the substance passes from green through blue and bluish-violet to violet and reddish-violet.

A. H.

**Halogen-additive Compounds from  $\alpha$ - and  $\beta$ -Naphthaquinone.** By T. ZINCKE and M. SCHMIDT (*Ber.*, 1894, 27, 2753—2762).—

$\alpha$ -Naphthaquinone dichloride,  $C_6H_4 < \begin{smallmatrix} CO \cdot CHCl \\ CO \cdot CHCl \end{smallmatrix}$ , is obtained by the direct action of chlorine on  $\alpha$ -naphthaquinone in acetic acid solution. It is very sparingly soluble in alcohol, and crystallises from benzene in colourless prisms, which melt and decompose at 176°. The dichloride is not affected by the continued action of chlorine or bromine, or of bleaching powder solution, but is slowly converted into chlorhydroxynaphthaquinone by alkalis. It readily loses hydrogen chloride, forming the chloro- $\alpha$ -naphthaquinone which melts at 117°; chlorine converts the latter into dichloronaphthaquinone, which can readily be prepared in this way.

$\alpha$ -Naphthaquinone dibromide forms broad, colourless tablets or plates, melts and decomposes at 92°, and resembles the chloride in its chemical properties. Brom- $\alpha$ -naphthaquinone, prepared by boiling the bromide with acetic acid and sodium acetate, forms small, compact crystals melting at 130°.

$\beta$ -Naphthaquinone dichloride,  $C_6H_4 < \begin{smallmatrix} CO-CO \\ CHCl \cdot CHCl \end{smallmatrix}$  + 2H<sub>2</sub>O, crystallises in white plates or broad needles, and melts at 86°. It readily loses hydrogen chloride, and is slowly converted by bleaching-powder

solution into the lactone of dichloro- $\beta$ -hydroxyorthocarboxyhydrocinnamic acid,  $\text{CO} < \overset{\text{O}}{\text{C}_5\text{H}_4} > \text{CH} \cdot \text{CCl}_2 \cdot \text{COOH}$  (Abstr., 1894, i, 289), chloro- $\beta$ -naphthaquinone being probably formed as an intermediate product.

Aqueous sulphurous acid converts the dichloride into monochloro- $\beta$ -naphthaquinol (Abstr., 1887, 53), which yields a *diacetate* melting at  $149^\circ$ .

When treated with aqueous soda, the dichloride is partially converted into chlorhydroxynaphthaquinone, and partially into *chlor-orthovinylbenzoylcarboxylic acid*,  $\text{COOH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{H}_2\text{Cl}$ , which crystallises in yellow needles, and melts at  $102\text{--}103^\circ$ . On oxidation, this acid yields *chlororthovinylbenzoic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CHCl}$ , which crystallises in scales, melts at  $151\text{--}152^\circ$ , and is converted by reduction into orthoethylbenzoic acid.

$\beta$ -Naphthaquinone dibromide forms small, yellow crystals, and melts and decomposes at  $65^\circ$ . It rapidly decomposes when kept, and loses hydrogen bromide when dissolved in alcohol. A. H.

**Tetrahydronaphthalic acid.** By C. ZENGELIS (*Ber.*, 1894, 27, 2694—2695).—When dihydronaphthalic acid (Anselm, Abstr., 1889, 717) is heated at  $140^\circ$  with hydriodic acid and phosphorus, it is further reduced to *tetrahydronaphthalic acid*,  $\text{C}_{10}\text{H}_{10}(\text{COOH})_2$ . This has no definite melting point, but at  $185^\circ$  begins to be converted into the *anhydride*, which melts at  $119.5^\circ$ , and dissolves in alkalis. The acid yields a *monethylic salt* melting at  $48^\circ$ , and also nitro-derivatives. Heating with sulphuric acid converts it into naphthalic anhydride.

C. F. B.

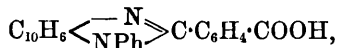
**Orthodiamines.** By O. FISCHER (*Ber.*, 1894, 27, 2773—2781; compare Abstr., 1893, i, 283).— $\beta$ -Phenylnaphthylene carbamide,



prepared from carbonyl chloride and  $\beta$ -phenyl-1 : 2-naphthylenediamine, crystallises in long, colourless prisms, melts at  $238^\circ$ , and exhibits a blue fluorescence in benzene solution. The stability of the compound towards acids and alkalis is in favour of the formula given above, but opposed to the alternative formula

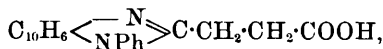


*n*-Phenylnaphthimidazole- $\beta$ -phenylorthocarboxylic acid,



obtained by the interaction of the diamine and phthalic anhydride, crystallises in colourless prisms, melts at  $260^\circ$ , and forms salts with both acids and bases. The *calcium salt* crystallises in stellate needles; the *picrate* is deposited in pale yellow prisms, and explodes at  $260^\circ$ . The *hydrochloride*,  $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_2 \cdot \text{HCl}$ , crystallises in lustrous needles.

*n*-Phenylnaphthimidazole- $\beta$ -propionic acid,



is formed by heating the diamine with succinic anhydride; it crystallises in reddish plates, melts at 180—181°, shows a blue fluorescence in benzene solution, and has both basic and acidic properties. The *hydrochloride* crystallises from alcohol in colourless needles, from hydrochloric acid in long prisms, and is dissociated by water. The *picrate* forms long yellow needles; the *silver salt* is colourless, pulverulent, and stable towards light.

The preparation of  $\alpha$ -ethyl- $\beta$ -phenylnaphthylenediamine has been previously described; the red dye which is formed as a bye-product, dissolves in concentrated sulphuric acid with a blue coloration, and is probably an oxidation product of phenylnaphthylenediamine. The *hydrobromide* crystallises in lustrous, bronze plates.

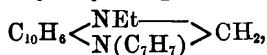
$\alpha$ -Ethyl- $\beta$ -phenylnaphthylenethiocarbamide,  $C_{10}H_8<\begin{smallmatrix} NEt \\ NPh \end{smallmatrix}>CS$ , formed by the action of carbon bisulphide on the diamine, is very sparingly soluble, crystallises in short, colourless prisms, and melts above 300°.

By the action of formic acid and zinc chloride, of chloral, or of commercial formaldehyde on the diamine, a *naphthimidazol derivative*,  $C_{10}H_8<\begin{smallmatrix} NEt \\ NPh \end{smallmatrix}>CH\cdot OH$ , is formed; it crystallises in colourless needles, melts at 161°, and its solutions fluoresce like petroleum; a fugitive blue coloration is obtained with concentrated sulphuric acid. The compound is stable towards acids and alkalis. The diamine reacts in the ordinary manner with acetic anhydride, and although the formation of the imidazol from formic acid is easily understood, its preparation from formaldehyde, which was almost free from acid, is difficult to explain. The *platinochloride*,  $(C_{10}H_8N_2O)_2\cdot H_2PtCl_6$ , crystallises in brownish-yellow needles, and dissociates in contact with water.

Paratolynaphthylenediamine has been previously described (Abstr., 1892, 1472); it melts at 146—147°. The *hydrochloride* crystallises in needles. On oxidation with lead oxide, the base yields a tolunaphthazine,  $C_{10}H_6<\begin{smallmatrix} N \\ N \end{smallmatrix}>C_6H_4Me$ , which has been previously prepared by Witt (Abstr., 1887, 591).

*n*-Paratolynaphthimidazole, formed by the interaction of the diamine and formaldehyde, crystallises in colourless prisms, and melts at about 200°. *Symmetrical ethylparatolyl-1 : 2-naphthylenediamine*,  $NHEt\cdot C_{10}H_8\cdot NHPh$ , obtained by the action of ethylic bromide on the diamine, crystallises in flat, colourless, lustrous needles, and melts at 68°. That it is a secondary base is shown by the formation of a *mononitrosamine*, which crystallises in yellow plates, and melts at 138°.

1 : *n*-Ethyl-2 : *n*-paratolyldihydronaphthimidazole,

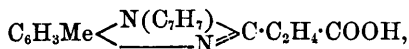


prepared from formaldehyde and the diamine, crystallises in colourless prisms, and melts at 175—178°. The compound is extremely stable, and is not acted on by dilute sulphuric acid at 150°; its solutions exhibit a blue fluorescence. 1-Benzyl-2-tolynaphthylenediamine is formed by the interaction of benzylic chloride and paratolyl-1 : 2-



naphthylenediamine; it crystallises from alcohol in pale yellow prisms, and melts at 157°. The *hydrochloride* crystallises in colourless, lustrous plates, melts at 204°, and its solutions, like those of the base, exhibit a blue fluorescence. The *acetyl derivative* is deposited from alcohol in colourless plates melting at 162°. 1 : *n*-Benzyl-2 : *n*-tolylidihydronaphthimidazole, formed by the action of formaldehyde on the base, crystallises from alcohol in colourless prisms, and melts at 125°.

The anhydro-base (m. p. 165—166°), previously obtained (*loc. cit.*) from benzaldehyde and orthamidoparaditolylamine, is also formed from benzoic chloride and orthamidoditolylamine. The *carboxylic acid*,  $\text{C}_6\text{H}_3\text{Me} \langle \text{N}(\text{C}_7\text{H}_7) \rangle \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$  [ $\text{NC}_7\text{H}_7 : \text{N} : \text{Me} = 1 : 2 : 4$ ], is prepared by heating phthalic anhydride with amidoditolylamine; it crystallises in colourless needles, melts at 173°, dissolves in alkalis, and is precipitated by acids. The acid,



formed in a similar manner from succinic anhydride and the amine, crystallises in slender, colourless needles melting at 228°.

Orthamidoditolylamine, when oxidised with lead oxide, yields a *ditolazine*,  $\text{C}_6\text{H}_3\text{Me} \langle \text{N} \rangle \text{C}_6\text{H}_3\text{Me}$  [ $\text{Me} : \text{N} : \text{N} = 1 : 3 : 4 ; 1 : 3 : 4$  or  $1 : 3 : 4 ; 1 : 4 : 5$ ]; the reaction is similar to the formation of phenazine from orthamidodiphenylamine. The compound crystallises in pale yellow needles, melts at 156°, and, with sulphuric acid, gives a blood-red coloration, changing to yellow when diluted.

J. B. T.

**Terpenes and Ethereal Oils.** By O. WALLACH (*Annalen*, 1894, 281, 127—147 and 147—166; compare *Abstr.*, 1891, 1240).—When limonene tetrabromide is warmed on the water bath with a solution of sodium in methylic alcohol, a *compound* is obtained which has the constitution  $\text{C}_{10}\text{H}_{14}\text{Br} \cdot \text{OMe}$ ; it boils at 137—140° (14 mm.); the sp. gr. = 1.251 at 18°, and  $n_D = 1.51963$  at the same temperature. When treated with hydrogen bromide in glacial acetic acid, it yields dipentene tetrabromide, and the action of sodium ethoxide gives rise to *carveol methyl ether*,  $\text{C}_{10}\text{H}_{15} \cdot \text{OMe}$ , an oil of pleasant odour, which boils at 210—212°, has a sp. gr. = 0.9065 at 18°, and a specific refractive index  $n_D = 1.47586$  at this temperature. On oxidation with chromic anhydride in glacial acetic acid solution, carveol methyl ether yields carvone, the transformation of limonene into carvone being thus effected. Terpeneol also may be converted into carvone in a similar manner, since the tetrabromide yields carveol methyl ether by the action of sodium methoxide. Cymene is formed when terpeneol tribromide is boiled with alcoholic potassium cyanide.

The author cannot confirm his former conclusion, that the dipentene dihydriodides described by him correspond with v. Baeyer's dihydrobromides and dihydrochlorides. The sole product of the action of phosphorus triiodide on terpin hydrate is the hydriodide,  $\text{C}_{10}\text{H}_{18}\text{I}_2$ , which melts at 70°.

Pinole dibromide is converted into cymene by energetic reducing agents, such as formic acid or zinc-dust and glacial acetic acid; the latter also gives rise to the diacetate of pinole glycol when boiled, whilst under other conditions solid terpineol is formed.

Pinole tribromide,  $C_{10}H_{17}OBr_3$  (compare Abstr., 1891, 218), is most conveniently prepared by treating pinole dibromide with hydrogen bromide in glacial acetic acid. When reduced in alcoholic solution with sodium, it yields a *compound* which boils at  $225^\circ$ ; the *oxime* melts at  $82-83^\circ$ . If reduction is effected by means of zinc-dust and glacial acetic acid, an unsaturated *ketone*,  $C_{10}H_{16}O$ , is formed, boiling at  $213-218^\circ$ ; the *secondary alcohol*,  $C_{10}H_{18}O$ , derived from this substance, boils at  $218-220^\circ$ , and has the specific rotatory power  $n_D = 1.47096$  at  $21^\circ$ , and the sp. gr. =  $0.91$  at the same temperature. The alcohol is very viscous, and has a pleasant odour resembling that of linalool and terpineol; the ketone is regenerated from it by oxidation.

The author discusses the constitution of pinole, representing it by the formula  $CH \begin{array}{c} \text{CMe} \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CPr} \end{array} \text{CH}_2 \text{O}$ .

M. O. F.

**Combination of Borneol, Camphor, and Monochlorcamphor with Aluminium Chloride.** By G. PERRIER (*Compt. rend.*, 1894, 119, 276—277).—When powdered borneol (2 mols.) is heated with anhydrous aluminium chloride (1 mol.) at about  $70-80^\circ$ , an energetic action takes place without liberation of hydrogen chloride, and the mixture partially liquefies. If the reaction is completed by heating at  $110-120^\circ$ , a homogeneous liquid is obtained which, on cooling, solidifies to a brownish-yellow crystalline mass. In presence of a small quantity of carbon bisulphide, the reaction takes place at the ordinary temperature, and a well-defined product is obtained in bulky crystals, but if a large proportion of the bisulphide is used, the yield is much lower. The product, which has the composition  $(C_{10}H_{18}O)_2 \cdot Al_2Cl_6$ , alters readily on exposure to air, and becomes rose-coloured by the action of light. Water decomposes it somewhat rapidly with separation of borneol and production of a solution of aluminium chloride. Hot benzene, toluene, and chloroform partially decompose it with liberation of hydrogen chloride.

Camphor, under the same conditions, yields an analogous compound,  $(C_{10}H_{16}O)_2 \cdot Al_2Cl_6$ , which crystallises in plates. It becomes red when exposed to light, and alters rapidly when exposed to air. It is decomposed by water with liberation of camphor. Monochlorcamphor, melting at  $97^\circ$ , also yields a product analogous in composition and properties.

Ferric chloride likewise combines with borneol, camphor, and monochlorcamphor, but the products have not yet been analysed.

C. H. B.

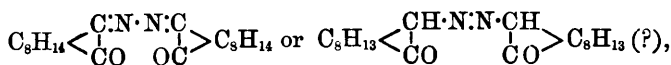
**Nitrocamphor.** By N. TARUGI (*Gazzetta*, 1894, 24, i, 528—531).—On reducing  $\beta$ -nitrocamphor melting at  $83^\circ$  with sodium in alcoholic solution, a *sodium* salt which is very soluble in water, but practically insoluble in concentrated soda, is obtained; it yields a yellow floccu-

lent substance on treatment with hydrochloric acid. This, when heated with acetic acid, is converted into  $\alpha$ -nitrocamphor, melting at 102—103°. W. J. P.

**Action of Nitrous acid on Amidocamphor.** By A. ANGELI (*Gazzetta*, 1894, 24, ii, 44—52).—Monoketoazocamphoquinone,  $C_8H_{14}<\begin{smallmatrix} \text{CN}_2 \\ \text{CO} \end{smallmatrix}>$  (Abstr., 1893, i, 570), behaves like a diazo-compound; on heating, it evolves nitrogen, leaving camphenone and azocamphanone.

Camphenone,  $C_{10}H_{16}O$ , separates from petroleum in colourless crystals melting at 168—170°; its oxime,  $C_{10}H_{15}NOH$ , crystallises in magnificent colourless plates melting at 132°.

Azocamphanone,



crystallises in lustrous scales melting at 222°.

W. J. P.

**Isocampholic acid.** By GUERBET (*Compt. rend.*, 1894, 119, 278—280).—The residue from the preparation of campholic acid by the author's method of heating camphor, sodiocamphor, and sodio-borneol in sealed tubes, contains another acid, *isocampholic acid*, which has the same composition.

The campholic acid is liberated by passing a current of carbonic anhydride through the faintly alkaline liquid, and the isocampholic acid is precipitated on adding hydrochloric acid. In order to purify it, it is dissolved in ether, dried over calcium chloride, the ether distilled off, and the residue mixed with its own weight of absolute alcohol and saturated with hydrogen chloride at 0°. Under these conditions, isocampholic acid yields an alkyl salt, whilst campholic acid does not. After remaining for 12 hours at the ordinary temperature, the liquid is treated with a large quantity of water, and the oily, supernatant liquid is decanted off, and washed with dilute sodium hydroxide solution to remove campholic acid. The ethylic isocampholate is dried over calcium chloride and fractionated. The portion boiling between 215° and 240° is hydrolysed by means of alcoholic potash, and the acid is converted into the calcium salt, which is purified by repeated crystallisations from absolute alcohol. It is then again converted into the ethylic salt, the fraction which boils between 228—229° is hydrolysed, and the free acid dried and distilled under reduced pressure.

Isocampholic acid,  $C_{10}H_{18}O_2$ , boils at 180—181°, under a pressure of 65 mm., and at 256—257° with partial decomposition under ordinary pressure; sp. gr. at 0° = 0.9941; rotatory power,  $[\alpha]_D = +24^\circ 38'$ ; vapour density = 4.90 (Cal. 5.88). The vapour density of the methylic salt, however, is 6.43 (Cal. 6.37), and of the ethylic salt 6.85 (Cal. 6.85). The acid is a colourless, oily liquid, with a disagreeable odour recalling that of valeric acid. It is almost insoluble in water, but is miscible with alcohol and ether. It does not

combine with bromine, and its salts crystallise readily from water, alcohol, or ether.

*Methylic isocampholate* is a colourless, oily liquid boiling at  $216-218^{\circ}$ ; sp. gr. at  $0^{\circ} = 0.9593$ . The *ethylic* salt is a colourless, oily liquid with a very disagreeable odour; sp. gr. at  $0^{\circ} = 0.9477$ .

*Isocampholamide*, obtained by heating the ammonium salt at  $210^{\circ}$  for six hours, crystallises from boiling water in nacreous plates, which are almost insoluble in cold water. It melts at  $116^{\circ}$ , and dissolves very readily in alcohol and in ether.

C. H. B.

**Hydroxymethylene Compounds.** By L. CLAISEN (*Annalen*, 1894, **281**, 306—313; compare next abstract and Abstr., 1893, i, 360, 480).—The formyl ketones are unstable substances, three molecules readily condensing to form a benzene derivative (Abstr., 1890, 357). They have the general formula  $R \cdot CO \cdot CH_2 \cdot COH$ , and homologues of them having the constitution  $R \cdot CO \cdot CHR \cdot COH$ , can easily be prepared. The behaviour of the formyl ketones towards ferric chloride may be used as a method of distinguishing between ketones containing the group  $-COMe$  or  $-CO \cdot CH_2R$  and those containing the group  $-CO \cdot CHR_2$  or  $-CO \cdot CR_3$ . The ketone, in ethereal solution, is treated with ethylic formate and sodium, the excess of sodium removed by adding alcohol, the solution acidified with acetic acid, and water added; the ethereal solution, when diluted with alcohol and treated with ferric chloride, turns red if a ketone of a primary acid is present, but only gives dull brownish-yellow colours with the ketones of secondary or tertiary acids. Acetone and its normal homologues, ethylic levulinate, mesitylic oxide, acetophenone, benzylideneacetone, and others, give the red colour; phenyl isopropyl ketone, benzophenone, phorone, and dibenzylideneacetone give feeble brown solutions readily distinguished from the former.

W. J. P.

**Hydroxymethylenecamphor.** By A. W. BISHOP, L. CLAISEN, and W. SINCLAIR (*Annalen*, 1894, **281**, 314—398; compare Abstr., 1893, i, 360, 480).—Hydroxymethylenecamphor or camphoraldehyde,

$C_8H_{14} < \begin{matrix} C:CH \cdot OH \\ CO \end{matrix}$  (compare Abstr., 1889, 619), crystallises in small,

colourless prisms melting at  $80-81^{\circ}$ ; it is very sparingly soluble in cold water, giving a solution which reddens litmus. It slowly and spontaneously changes to an amorphous, pasty mass, which is converted into the crystalline modification on distillation in a current of steam. It is soluble in soda, and only partially and slowly precipitated from the solution by carbonic anhydride. The *ammonium* and *potassium* salts were prepared, and also a *copper* salt of the composition  $(C_{11}H_{15}O_2)_2Cu \cdot 2C_{11}H_{15}O_2$ , which crystallises in silky needles melting at  $126^{\circ}$ . The *ferric* salt,  $(C_{11}H_{15}O_2)_3Fe$ , crystallises in dark violet leaflets, and partially sublimes when heated in a vacuum; it converts potassium cyanide into ferrocyanide in dilute alcoholic solution. Although the salt is insoluble in water, yet, after adding ferric chloride to its alcoholic solution, the latter is no longer precipitated by water; in place of a salt of the composition  $FeR_3$ , one of

the composition  $\text{FeRCl}_2$  or  $\text{FeR}_2\text{Cl}$  is probably formed, although it could not be isolated.

Hydroxymethylenecamphor yields camphor and sodium formate on hydrolysis with soda, bromocamphor melting at  $75-76^\circ$  on treatment with bromine, and camphoric acid on oxidation with alkaline permanganate; when oxidised with chromic acid, it gives camphororthoquinone. On adding diazobenzene chloride to its soda solution, camphoquinonemonophenylhydrazone separates; hydroxylamine hydrochloride acts on the soda solution yielding a colourless viscous liquid which slowly turns brown and blue, and is probably either formylcamphoroxime or hydroxymethylenecamphorhydroxylamide. If the hydroxylamine is added to the heated solution, cyanocamphor is obtained; this process should be a very convenient one for preparing the latter substance.

*Hydroxymethylenecamphorphenylpyrazole*,  $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix} \text{C}-\text{CH} \\ | \\ \text{C}\cdot\text{NPh} \end{smallmatrix}\rangle\text{N}$ , is prepared by warming hydroxymethylenecamphor with phenylhydrazine in acetic acid solution; it crystallises in monosymmetric plates or prisms, melting at  $124-125^\circ$ ;  $a : b : c = 1.8956 : 1 : 1.3478$ .  $\beta = 115^\circ 43'$ .

*Amidomethylenecamphor*,  $\text{C}_{10}\text{H}_{14}\text{O}:\text{CH}\cdot\text{NH}_2$ , is obtained by treating the hydroxy-derivative with ammonia; it crystallises in colourless, lustrous leaflets melting at  $164-165^\circ$ . It dissolves completely in dilute hydrochloric acid, but the solution immediately deposits a mixture of hydroxymethylenecamphor and *imidomethylenecamphor*,  $\text{NH}(\text{CH}\cdot\text{C}_{10}\text{H}_4\text{O})_2$ . The latter is most conveniently prepared by melting amido- and hydroxy-methylenecamphor together, and is also formed by heating chloromethylenecamphor with excess of methylic alcoholic ammonia at  $100^\circ$ ; it crystallises in minute cubes melting at  $220-221^\circ$ .

*Anilidomethylenecamphor*,  $\text{C}_{10}\text{H}_{14}\text{O}:\text{CH}\cdot\text{NHPh}$ , crystallises in lustrous prisms melting at  $167-170^\circ$ ; it may be prepared by heating ethoxymethylenecamphor or chloromethylenecamphor with aniline. The corresponding *paratoluido*-derivative crystallises in thin prisms melting at  $188-189^\circ$ . *Methylanilidomethylenecamphor*,



crystallises in lustrous orthorhombic prisms melting at  $124^\circ$ ;  $a : b : c = 0.792 : 1 : 0.7535$ .

*Chloromethylenecamphor*,  $\text{C}_{10}\text{H}_{14}\text{O}:\text{CHCl}$ , prepared by the action of phosphorus trichloride on hydroxymethylenecamphor, is a colourless oil of camphor-like odour; it has a sp. gr. of 1.09 at  $15^\circ$ , boils at  $241-242^\circ$ , and melts at  $11-12^\circ$ . It is accompanied by *hydroxymethylenecamphor hydrogen phosphite*,  $\text{C}_{10}\text{H}_{14}\text{O}:\text{CH}\cdot\text{O}\cdot\text{P}(\text{OH})_2$ , which crystallises in colourless needles melting at  $113-115^\circ$ . *Bromomethylenecamphor* crystallises in long needles melting at  $31-32^\circ$ , and boils at  $260-261^\circ$ .

On heating the potassium derivative of hydroxymethylenecamphor, an *anhydride*,  $(\text{C}_{10}\text{H}_{14}\text{O}:\text{CH})_2\text{O}$ , is obtained; it crystallises in lustrous monosymmetric plates melting at  $188-189^\circ$ ;  $a : b : c =$

1.9105 : 1 : 1.8011.  $\beta = 96^\circ 35.5'$ . It boils without decomposition, and is readily hydrolysed by alcoholic potash.

The alkylic derivatives of hydroxymethylenecamphor are readily obtained by the usual methods; the following have been prepared.

*Methoxymethylenecamphor*,  $C_{10}H_{14}O:CH \cdot OMe$ , crystallises in prisms melting at  $40^\circ$ ; it boils at  $262^\circ$ . The corresponding *ethoxy*-compound is a colourless oil boiling at  $269$ — $270^\circ$ , and having a sp. gr. = 1.007 at  $15^\circ$ . The *benzyloxy*-derivative forms a colourless crystalline mass melting at  $45$ — $46^\circ$ , and boiling at  $222$ — $224^\circ$  under 15 mm. pressure. The *phenoxy*-derivative is a colourless, viscid oil which boils at  $320^\circ$  undergoing slight decomposition. These substances are readily hydrolysed by fuming hydrobromic acid in the cold, showing that they are true alkyloxy-derivatives.

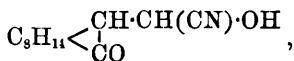
*Acetoxymethylenecamphor*,  $C_{10}H_{14}O:CH \cdot OAc$ , melts at  $63$ — $64^\circ$ , and boils at  $290$ — $293^\circ$ ; on prolonged heating with alcoholic sodium ethoxide, it yields the hydroxy-derivative.

Two, probably stereoisomeric, benzoyl-derivatives of hydroxymethylenecamphor can be prepared.  $\alpha$ -*Benzoxymethylenecamphor*,



is obtained by heating benzoic chloride with hydroxymethylenecamphor at  $140$ — $160^\circ$ ; by warming an alcoholic solution of the latter with sodium ethoxide and benzoic chloride; by the action of benzoic chloride on the sodio-derivative of the hydroxy-compound suspended in ether; or by adding benzoic chloride to a soda solution of the hydroxy-compound. It crystallises in six-sided orthorhombic plates melting at  $119$ — $120^\circ$ , and boils without much decomposition at  $370^\circ$ ;  $a : b : c = 0.5767 : 1 : 1.3814$ .  $\beta$ -*Benzoxymethylenecamphor* is obtained together with the  $\alpha$ -modification by the action of benzoic chloride on sodium ethoxide and the hydroxy-compound in ethereal solution at  $-15^\circ$ ; it crystallises in large, lustrous monosymmetric crystals melting at  $91$ — $92^\circ$ ;  $a : b : c = 1.0679 : 1 : 0.9946$ .  $\beta = 119^\circ 8'$ . The  $\alpha$ -isomeride has the specific rotations  $[\alpha]_D = +139.02^\circ$  and  $140.68^\circ$  in 4.5 and 13.5 per cent. benzene solutions at  $20^\circ$ ; under similar conditions, the  $\beta$ -modification has the specific rotations  $[\alpha]_D = +159.3^\circ$  and  $161.9^\circ$ . The  $\beta$ -modification is converted into the  $\alpha$ -form by heating its alcoholic solution with a little hydrochloric acid, or by distilling it; the  $\beta$ -modification cannot be converted into the  $\alpha$ -isomeride. Both forms give the same hydroxymethylenecamphor when heated with alkalis. If, during the preparation of the benzoyl-derivative in alcoholic sodium ethoxide solution, the temperature be allowed to rise, ethylic benzoate is produced.

*Cyanomethylenecamphor*,  $C_{10}H_{14}O:CH \cdot CN$ , is prepared by treating the chloro- or hydroxy-derivative with potassium cyanide in methylic alcohol solution; it forms a crystalline mass melting at  $46$ — $47^\circ$  and boiling at  $279$ — $282^\circ$ . In the action of potassium cyanide or hydrocyanic acid on hydroxymethylenecamphor, the *cyanhydrin*,



of the latter is formed; it crystallises in silky needles melting at 122—123°, has a feebly acid reaction, and is converted into the cyano-derivative on heating with acetic anhydride.

*Methylenecamphorcarboxylic acid*,  $C_{10}H_{14}O \cdot CH \cdot COOH$ , is obtained by hydrolysing the cyano-derivative with hydrochloric acid; it crystallises in compact prisms melting at 100—102°, distils and slightly carbonises at 320°, and is soluble in hot water. The *silver* salt is a white powder, and the *methylic* salt melts at 62—63°. The acid yields

a compound,  $C_8H_{14} < \begin{array}{c} C \cdot CO \cdot O \cdot C \\ | \quad | \\ H \quad H \\ C \cdot O \cdot CO \cdot C \end{array} > C_8H_{14}$  (?), on heating with acetic chloride; this substance has the normal molecular weight in boiling benzene or nitrobenzene solution, and crystallises in small, colourless needles melting at 195—196°.

*Hydroxymethylenementhone*,  $C_8H_{16} < \begin{array}{c} C \cdot CH \cdot OH \\ | \\ CO \end{array} >$ , is prepared by the action of sodium and amylic formate on an ethereal solution of menthone; it is a colourless oil of agreeable odour boiling at 250—252°, and having a sp. gr. = 1.002 at 15°. The *sodio*-derivative crystallises in colourless leaflets or prisms. It is very readily hydrolysed in alkaline solutions yielding menthone and formic acid.

*Acetoxymethylenementhone*,  $C_{10}H_{16}O \cdot CH \cdot OAc$ , is a colourless oil boiling at 160—162° under 12—13 mm. pressure. The *benzoxy*-derivative crystallises in white leaflets melting at 75—76°. The *methoxy*-derivative (?), which boils at 250—260°, is formed together with *methylenementhone*,  $C_{10}H_{17}MeO$ , boiling at 213—215°, by the action of methylic iodide and sodium methoxide on hydroxymethylenementhone.

An improved method for preparing hydroxymethylenepropyl phenyl ketone is given; it melts at 87—89°, and boils at 260—262° with slight decomposition. The *acetoxymethylenepropyl phenyl ketone*,  $COPh \cdot CEt \cdot CH \cdot OAc$ , is a colourless oil boiling at 167—168° under 13 mm. pressure. The *methylanilide*,  $COPh \cdot CEt \cdot CH \cdot NMePh$ , crystallises in white needles melting at 72—73°.

*Methylic hydroxymethylenephenylacetate* is a colourless, viscous oil boiling at 135—136° under 14 mm. pressure. The *acetoxymethylenephenylacetate*,  $CPh(COOMe) \cdot CH \cdot OAc$ , is an oil boiling at 176° under 16—17 mm. pressure.

W. J. P.

**Digitogenin Derivatives.** By H. KILIANI and M. BAZLEN (*Arch. Pharm.*, 1894, **232**, 334—345; compare *Abstr.*, 1893, i, 665).—Digitogenic acid is prepared from digitogenin by treating it with glacial acetic acid (10 parts) and subsequently oxidising with chromic anhydride (0.7 part) dissolved in water (1.4 parts). After further dilution with water (10 parts), the acid is extracted by means of ether. This method is less costly and troublesome than the one formerly described, and the yield is the same. *Digitogenic acid oxime*,  $C_{14}H_{21}O_3N$ , crystallises in needles or prisms, melts at 175°, has an acid reaction, and dissolves in sodium carbonate with evolution of carbonic anhydride. The *magnesium salt*  $(C_{14}H_{21}O_3N)_2Mg$  and the *barium salt* are crystalline, the latter being deposited in needles.

Attempts to prepare ethereal salts of digitic acid and acetyl- $\beta$ -anhydrodigitic acid (see below) were unsuccessful; *ethylic digitoate* crystallises in needles or prisms, commences to soften at  $120^{\circ}$ , and melts at about  $160^{\circ}$ . Attempts to prepare isopyrocampaenic acid, for comparison with the author's bibasic acid  $C_9H_{10}O_4$  (*loc. cit.*), failed; the latter compound is readily oxidised when heated with potassium permanganate; by the action of more concentrated potassium permanganate solution at ordinary temperatures, *digic acid*,  $C_8H_{12}O_3$ , is formed; this is deposited in granules, and softens at about  $130^{\circ}$ . The *calcium salt*  $(C_8H_{11}O_3)_2Ca + 6H_2O$ , crystallises in needles or prisms; the anhydrous salt is extremely hygroscopic. The *barium salt* is also crystalline.  $\alpha$ -*Anhydrodigitic acid*,  $C_{10}H_{14}O_3$ , is obtained by the action, at low temperatures, of hydrogen chloride in glacial acetic acid solution on digitic acid; it melts and decomposes at about  $245^{\circ}$ , gives a red coloration changing to greenish-yellow with concentrated sulphuric acid, and readily decolorises potassium permanganate solution, digitic acid being regenerated. The acid forms an additive compound with bromine, and gives with hydrogen iodide in glacial acetic acid solution, an iodine derivative, which combines with aniline; the resulting compound contains nitrogen and, in glacial acetic acid solution, gives a violet-red dye on exposure to the air. The alkali salts yield amorphous precipitates with calcium chloride; the *potassium salt*, when treated successively with alcohol and calcium chloride, forms a crystalline compound, which decomposes when dry. *Acetyl- $\beta$ -anhydrodigitic acid*,  $C_{10}H_{13}O_3Ac + H_2O$ , is prepared by the action of hydrogen chloride on  $\alpha$ -anhydrodigitic acid in presence of glacial acetic acid and acetic anhydride; it crystallises in needles or prisms, softens at  $140^{\circ}$ , and melts at  $170^{\circ}$ ; it reacts with sulphuric acid like  $\alpha$ -anhydrodigitic acid.  $\beta$ -*Anhydrodigitic acid* is prepared from the preceding compound by hydrolysing it with potash; it crystallises in long, lustrous, colourless needles, melts and decomposes at  $262$ – $263^{\circ}$ , and turns yellow on exposure to light and air. The *silver salt* was prepared. The formation of acetyl- $\beta$ -anhydrodigitic acid probably depends on the production of acetic chloride from the acetic anhydride and hydrogen chloride, and points to the existence of the group  $C \cdot O \cdot C$  in  $\alpha$ -anhydrodigitic acid, and presumably, also, in digitic acid.

J. B. T.

**Presence of Several Distinct Chlorophylls in the Same Vegetable Species.** By A. ÉTARD (*Compt. rend.*, 1894, 119, 289–291).—Amongst the products of the extraction of leaves by carbon bisulphide are monohydric and polyhydric alcohols of high molecular weight, which retain chlorophyll with great tenacity, and can be repeatedly crystallised from acetic acid and other solvents without losing their colour. According to the author, the substances that have been called “hypochlorin” and chlorophyllan are mixtures of this kind.

Leaves of lucerne (*Medicago sativa*) were collected shortly before inflorescence, dried in the dark, and extracted with carbon bisulphide. The residue was treated with alcohol of  $85^{\circ}$ , which dissolves extractive matters, glucoses, &c., yielding a solution with a very intense



green colour. After distilling off the alcohol, the residue is completely soluble in carbon bisulphide.

The yield is about 20 kilos of colouring matter per hectare of lucerne, and hence 2 grams of active matter per square metre at a height of 0.3 metre is sufficient to ensure the growth of the plant.

From the carbon bisulphide and alcoholic extracts, the author has separated four distinct and definite chlorophylls, which have been analysed, and will be described subsequently.

One of these has the composition  $C_{28}H_{45}NO_4$ , and cryometric determinations give for its molecular weight 425 (Cal. 459). The author distinguishes it by the name *α-medicago-phyll*. In order to isolate it, the solid extract is macerated with cold alcohol, and the residue from the alcoholic solution thus obtained is treated with ether. The latter is distilled off and the residue treated with pentane, which at first, owing to the presence of traces of ether, dissolves all the chlorophyll, but on the addition of more pentane, a portion of the colouring matter is precipitated and remains permanently insoluble in this solvent. The product is soft and amorphous, with bluish reflection, and great tinctorial power. It is soluble in carbon bisulphide but insoluble in water, and is free from extractive matters, gum, tannin, glucoses, and vegetable acids, and only leaves 0.88 per cent. of ash. Its solution in glacial acetic acid has an intense green colour with red dichroism. *α-Medicagophyll* is heavier than water. It is insoluble in concentrated potassium hydroxide solution, but dissolves in very dilute solutions of alkalis, from which it is precipitated by acids and even by sodium chloride. When dissolved in dilute potassium hydroxide solution, and heated with ammoniacal silver nitrate, it yields a silver mirror, a reaction which is shared by all the chlorophylls examined by the author.

C. H. B.

**Carminic acid.** By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, 1894, 27, 2979—2985; compare v. Miller and Rohde, *Abstr.*, 1894, i, 94).—Pure carminic acid is prepared by treating cochineal extract with lead acetate, decomposing the lead salt with sulphuric acid in presence of alcohol, and evaporating to dryness at the lowest possible temperature; the residue agrees in properties with the “carminic acid” described by others, and is further purified by dissolving it in cold absolute alcohol and precipitating with ether, benzene, or chloroform. It then crystallises from alcohol, at the ordinary temperature, in small, red prisms. Aqueous solutions of carminic acid, when evaporated, give an amorphous substance, but no crystals. Crystallised carminic acid,  $C_{11}H_{12}O_6$  or  $C_{11}H_8O_4 + 2H_2O$ , differs little in properties from the amorphous preparations, it darkens at 130°, and blackens without melting at 205°. In alcoholic solution, it shows three ill-defined absorption bands, one in the green and two in the blue; in alkaline solution, they appear in the yellow and green. The *barium* and *calcium* salts are brown, changing to violet with excess of base; the *lead* and *aluminium* salts are also violet, and the *stannous* salt scarlet. Aqueous carminic acid solutions are immediately decolorised by animal charcoal, the latter increasing greatly in volume and becoming gelatinous; this peculiar compound is not

changed by alcohol, but is decomposed into its constituents by alkalis. The *anilide*,  $C_{17}H_{13}O_3N + 3H_2O$ , is deposited in ruby crystals, darkens at  $130^\circ$ , melts and decomposes at  $189-190^\circ$ , and is hydrolysed by alkalis. It is impossible, at present, to decide in what manner the water is combined in the molecule. J. B. T.

**Filicic Acid.** By G. DACCOMO (*Gazzetta*, 1894, **24**, i, 511—523; compare Schiff, *Abstr.*, 1890, 162).—Copper filicate is obtained as a green, crystalline powder; it has the composition  $C_{28}H_{30}O_{10}Cu$ , and not that attributed to it by Grabowski (*Annalen*, **143**, 279). The *ammonium* salt,  $C_{14}H_{16}O_5 \cdot NH_4$ , is a white, amorphous powder having no definite melting point.

On oxidation with hydrogen peroxide, filicic acid yields an *acid*,  $C_{14}H_{16}O_6$ ; it is a red, amorphous powder, and does not reduce ammoniacal silver nitrate solution. The *potassium* salt,  $C_{14}H_{15}O_6K$ , is a reddish, crystalline powder, and is very soluble in water or alcohol. On oxidising filicic acid with potassium permanganate, nitric acid, bromine, or iodine, butyric acid is obtained together with a bibasic acid,  $C_8H_8O_4$ , which is probably dimethylmalonic acid. W. J. P.

**Action of Nascent Bromine on Pyrroline, Pyridine, and Pyrazole.** By W. VAUBEL (*J. pr. Chem.*, 1894, [2], **50**, 367—369).—Pyrroline reacts with rather more than 3 atoms of nascent bromine, the action of the latter being greatly hindered by the polymerisation of the pyrroline. Pyridine and its derivatives, including piperidine, are scarcely attacked, whilst pyrazole, according to the researches of Buchner (*Abstr.*, 1893, i, 432), reacts with 1 atom of bromine. These results are all in accordance with the author's theory of the configuration of the benzene molecule. Phenylpyrazole, on the other hand, according to Balbiano (*Abstr.*, 1893, i, 672), takes up 3 atoms of bromine. A. H.

**Synthesis of Pyrroline Compounds from Nitrosoketones.** By C. U. ZANETTI and E. LEVI (*Gazzetta*, 1894, **24**, i, 546—554).—*Ethyllic 2:4-dimethyl-3-acetylpyrroline-5-carboxylate*,  $C_9H_{14}EtO_3N$ , is prepared by treating ethylic acetoacetate dissolved in acetic acid with half the quantity of potassium nitrite necessary to convert it into the nitroso-derivative, adding acetylacetone, and then reducing the product with zinc-dust. It crystallises in lustrous white needles, melts at  $143^\circ$ , and gives a red coloration with dilute mineral acids; the corresponding *acid*, which is obtained on hydrolysis with potash, crystallises in acicular tufts melting at  $208-210^\circ$  with evolution of gas. The solution of the ammonium salt gives precipitates with lead, copper, ferric, mercuric, and barium salts.

2:4-Dimethyl-3-acetylpyrroline,  $NH \begin{array}{c} \text{CMe} \cdot \text{CAc} \\ \diagup \quad \diagdown \\ \text{CH} - \text{CMe} \end{array}$ , is obtained by distilling the above carboxylic acid; it crystallises in white lustrous needles, melts at  $139-140^\circ$ , and is very soluble in alcohol, ether, ethylic acetate, less so in boiling water, and insoluble in solutions of alkali carbonates. It acts as a feeble base, dissolving in concentrated hydrochloric acid, but separating again on dilution.

On heating the carboxylic acid with acetic anhydride, a *tetramethyl-*

*diacetylpyrocolline*,  $C_4Me_2Ac \begin{smallmatrix} \text{CO}\cdot\text{N} \\ \text{N}\cdot\text{CO} \end{smallmatrix} C_4Me_2Ac$ , is formed; it crystallises in long, yellowish needles melting at  $206-208^\circ$ , with slight decomposition, and very sparingly soluble. It has the normal molecular weight in freezing acetophenone. It is hydrolysed by boiling alkalis with re-formation of the acid.

On treating acetylacetone in acetic acid solution with sodium nitrite, adding ethylic acetoacetate and reducing the product with zinc-dust, ethylic 2:4-dimethyl-5-acetylpyrroline-3-carboxylate is obtained isomeric with the ethylic salt first described; the corresponding acid melts at  $252-254^\circ$ , the lower temperature given by Magnanini being due to a printer's error. W. J. P.

**Königs and Lellmann's Hydroquinoline.** By V. VINCENZI (*Gazzetta*, 1894, **24**, ii, 97—100).—Königs dihydroquinoline,  $(C_9NH_9)_2$ , prepared by reducing quinoline with zinc-dust and ammonia, seems to be a mixture of two isomerides. By extracting the product with alcohol, two yellow amorphous dihydroquinolines can be obtained melting at  $172-174^\circ$  and  $184-187^\circ$  respectively; it is not yet clear whether these substances are identical or isomeric. They both have the normal molecular weight in freezing benzene or acetic acid.

On treatment with nitrous acid, the dihydroquinoline yields a *nitrosamine* which gives Liebermann's reaction. On brominating, the substance melting at  $184-187^\circ$ , an *additive* product,  $C_9NH_9Br(?)$ , is obtained. W. J. P.

**Dihydroquinolines.** By A. FERRATINI (*Gazzetta*, 1894, **24**, ii, 190—196; compare Abstr., 1893, i, 602).—The properties of the dihydroquinolines, as would be expected, resemble those of the indoles rather than those of the quinolines. It was therefore to be supposed that the trimethyldihydroquinoline prepared by the author (Abstr., 1893, i, 227) would behave like the methylindoles; this was found to be the case, as the hydrogenated quinoline gives the reactions which E. Fischer and P. Wagner (Abstr., 1888, 283) discovered to hold for methylketoles.

*Acetyltrimethyldihydroquinoline*,  $C_9NH_9Me_3Ac$ , is obtained on boiling trimethyldihydroquinoline with sodium acetate and acetic anhydride; it crystallises from light petroleum in long, colourless, prismatic needles melting at  $100.5-101.5^\circ$  and is readily soluble in dilute acids. It yields an unstable *aurochloride* and a stable *platinochloride*,  $(C_{14}H_{17}NO)_2 \cdot H_2PtCl_6$ , which crystallises in yellow needles melting and decomposing at  $203-204^\circ$ . The acetyl-derivative is hydrolysed by hot concentrated acids but not by boiling potash.

*Benzilidenetrimethyldihydroquinoline*,  $CHPh(C_9NH_9Me_3)_2$ , is prepared by warming the quinoline with benzaldehyde; it is a white crystalline substance melting at  $142-144^\circ$ .

*Trimethyldihydroquinolineazobenzene*,  $C_9NH_9Me_3 \cdot N_2Ph$ , may be prepared by treating trimethyldihydroquinoline with diazobenzene chloride at  $0^\circ$ . It decomposes on exposure to the air, and yields a *picrate*,  $C_{24}H_{22}N_6O_7$ , which crystallises in red needles melting and decomposing at  $208-209^\circ$ . W. J. P.

**Synthesis of Kynurine.** By F. WENZEL (*Monatsh.*, 1894, 15, 453—468).—The investigations of Kretschky (*Abstr.*, 1881, 827; 1883, 674) have shown that kynurine is a hydroxyquinoline, the hydroxyl group of which is contained in the pyridine ring, and its presence in the oxidation products of cinchonic acid (*Abstr.*, 1887, 164; *Monatsh.*, 1887, 8, 801, 818) renders it probable that it is a 4'-derivative. In order to obtain a satisfactory proof of its constitution, the author has endeavoured to prepare kynurine synthetically from cinchonic acid, and has succeeded in doing so by a series of reactions, each of which proceeds almost quantitatively.

The starting point for the preparation of kynurine is ethylic cinchonate, which may be prepared by heating potassium cinchonate with potassium ethylic sulphate at 170—180°, but is best obtained by saturating the alcoholic solution of cinchonic acid with hydrogen chloride, the yield being almost quantitative if the excess of alcohol and hydrogen chloride are evaporated off in a vacuum. Ethylic cinchonate, contrary to the statement of van der Kolf and van Leent (*Abstr.*, 1889, 1017), distils without decomposition under 15 mm. pressure at 173°, and then forms a colourless, dispersive liquid which becomes pink after a time. It is best converted into cinchonamide by heating with alcoholic ammonia at 140—150°, the amide being thus obtained in lustrous, colourless needles melting at 178°.

When cinchonamide is treated with bromine and caustic potash, according to Hoogewerff and van Dorp's method, it is converted into 4'-amidoquinoline, a small quantity of *bromo-4'-amidoquinoline* being simultaneously formed. The latter crystallises in colourless, slender needles, sublimes at 105°, and melts, when quickly heated, at 199°. The properties of 4'-amidoquinoline observed by the author agree with those given by Hoogewerff and van Dorp. When treated with nitrous acid it does not yield a diazo-derivative, but is at once converted into 4'-chloroquinoline (compare Marckwald, *Abstr.*, 1894, i, 381), which melts at 29—30° (uncorr.) and boils at 260—261° (corr.) under 744 mm. pressure. It is identical with the chloroquinoline obtained by Skraup by the action of phosphorus pentachloride on kynurine, thus proving that the hydroxyl-group in the latter occupies the 4'-position. To further confirm this, the chloro derivative was converted into the ethyl derivative by heating it with alcoholic sodium ethoxide at 120°, and the ethyl derivative then heated with hydrochloric acid at 190°. The substance thus obtained was proved to be identical with kynurine both by its melting point and crystallographic form.

The *ethylykynurine*, prepared in the above manner, is a colourless oil, which boils at 186.5° under 30 mm. pressure, and possesses basic properties; its *platinochloride*,  $C_8NH_6OEt.H_2PtCl_6$ , crystallises with 2H<sub>2</sub>O in small, prismatic crystals, and melts, after drying, at 213°, and the *aurochloride*,  $C_8NH_6OEt.HAuCl_4$ , with 1H<sub>2</sub>O in small lustrous needles melting at 169°. On treatment with hydriodic acid, according to Zeisel's method, it yields no ethylic iodide, and, therefore, contains no ethoxy-group; hence it must be the *pseudo-ethylic* deriva-

tive  $C_8H_4 \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{N} \end{smallmatrix}$ . An attempt to obtain the ethoxy-derivative by the action of ethylic iodide on the silver compound of kynurine only

resulted in the formation of the pseudo-derivative, and it is therefore probable that kynurine in alkylation always reacts in the tautomeric form,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{NH} \cdot \text{CH} \end{smallmatrix}$ . It appears not improbable that the ketodihydroquinoline, described by Reissert (Abstr., 1888, 276, 694), is identical with kynurine. H. G. C.

**Action of Formaldehyde on Quinaldine.** By T. METHNER (Ber., 1894, 27, 2689—2693).—When quinaldine is heated at  $100^\circ$  in a sealed tube with an aqueous solution of formaldehyde, *quinaldinealkine*,  $C_9NH_5 \cdot CH_2 \cdot CH_2 \cdot OH$ , is formed. The free base melts at  $94-95^\circ$ ; the yellow *aurochloride* at  $134-135^\circ$ , turning red; the orange *platinochloride* at  $208-209^\circ$ , turning brown at  $200^\circ$ ; and the *mercurichloride*,  $C_{11}H_{11}NO \cdot HCl + 3HgCl_2$ , at  $135-136^\circ$ . If the alkine is heated with strong sulphuric acid and acetic acid at  $150-160^\circ$ , it yields *vinylquinoline*,  $C_9NH_5 \cdot CH \cdot CH_2$ , which was only obtained as an impure oil; the yellow *aurochloride* sinters to a green mass at  $113-114^\circ$ , and melts and decomposes at  $152-153^\circ$ ; the orange *platinochloride* turns black at  $182^\circ$ ; the *mercurichloride*,  $C_{11}H_9N \cdot HHgCl_2$ , melts at  $151-152^\circ$ , turning red. When the alkine is reduced with tin and hydrochloric acid, tetrahydroquinaldine is formed.

C. F. B.

**$\alpha$ -Alkylcinchonic acids and  $\alpha$ -Alkylquinolines: Carboxy- and Hydroxy-derivatives of  $\alpha$ -Phenylcinchonic acid.** By O. DOEBNER and H. FETTBACH (Annalen, 1894, 281, 1—15; compare Abstr., 1888, 299; 1889, 410).— $\alpha$ -Alkylcinchonic acids are formed when a mixture of an aldehyde and pyruvic acid is heated with an aromatic amine; compounds have been obtained in this way from orthamidobenzoic acid and ortho- and par-amidophenols.

*2'-Phenylquinoline-1:4'-dicarboxylic acid*,  $C_9NH_4Ph(COOH)_2$ , is prepared by heating a mixture of benzaldehyde, pyruvic acid, and orthamidobenzoic acid in alcoholic solution for six hours; it forms minute, colourless needles which melt and decompose above  $300^\circ$ . The *silver* salt is anhydrous, and the *magnesium* salt crystallises with  $1H_2O$ . Carbonic anhydride is eliminated when the acid is heated with soda-lime, with formation of  $\alpha$ -phenylquinoline.

No quinoline derivative can be obtained in this way from par-amidobenzoic acid, the compound formed having the constitution  $COOH \cdot C_6H_4 \cdot NH \cdot CO \cdot C(CH_3 \cdot CHPh) \cdot N \cdot C_6H_4 \cdot COOH$ . It is almost insoluble in alcohol, but may be recrystallised from glacial acetic acid, separating from it in minute needles which melt and decompose above  $300^\circ$ . The analogous *meta*-derivative closely resembles it in properties.

*1-Hydroxy-2'-phenylquinoline-4'-carboxylic acid*,  $OH \cdot C_9NH_4Ph \cdot COOH$ , is formed from orthamidophenol in the manner already indicated. It is deposited from glacial acetic acid in lustrous yellow needles which melt at  $247^\circ$ ; the *silver*, *copper*, and *calcium* salts are well defined substances.

*1-Hydroxy-2'-phenylquinoline* is formed when carbonic anhydride is eliminated from the foregoing acid by distillation; it crystallises from

methylic alcohol in quadratic plates and melts at 59°. The *platinochloride* crystallises in dark yellow needles, and the *picrate* separates from alcohol in yellow needles which melt at 152°.

*3-Hydroxy-2'-phenylquinoline-4'-carboxylic acid* is obtained from paramidophenol. Recrystallised from dilute hydrochloric acid, it contains 1 mol. H<sub>2</sub>O; fusion does not occur below 320°. The *silver* salt is unstable, and the *calcium*, *lead*, and *copper* salts are well defined. When distilled, the acid yields *3-hydroxy-2'-phenylquinoline*, which crystallises from water in slender, white needles melting at 218°. The *picrate* melts at 201°. M. O. F.

**$\alpha$ -Alkylcinchoninic acids and  $\alpha$ -Alkylquinolines: Amido-derivatives of  $\alpha$ -Phenylcinchoninic acid.** By O. DOEBNER and E. FERBER (*Annalen*, 1894, **281**, 15—24).— $\alpha\alpha'$ -Diphenylphenanthroline- $\gamma\gamma'$ -dicarboxylic acid,  $\text{CH} \begin{smallmatrix} \text{CPh}=\text{N} \\ \text{C}(\text{COOH}) \end{smallmatrix} > \text{C}_6\text{H}_2 < \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{C}(\text{COOH}) \end{smallmatrix} > \text{CH}$ , is obtained by heating a mixture of benzaldehyde and pyruvic acid with metaphenylenediamine hydrochloride in alcoholic solution for three hours. It separates from hot alcohol in minute, reddish-brown needles which melt at 235°. The *silver* salt decomposes at 100°. The *zinc* salt contains 1H<sub>2</sub>O, and the *magnesium* salt is a reddish-yellow powder of the composition C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Mg + MgO.

$\alpha\alpha'$ -Diphenylphenanthroline,  $\begin{smallmatrix} \text{CPh:N} \\ \text{CH:CH} \end{smallmatrix} > \text{C}_6\text{H}_2 < \begin{smallmatrix} \text{N:CPh} \\ \text{CH:CH} \end{smallmatrix}$ , is formed when the foregoing acid is distilled with soda-lime. The *platinochloride* decomposes at 100°.

*2-Dimethylamido-2'-phenylquinoline-4-carboxylic acid*,



is prepared by heating the mixed alcoholic solutions of benzaldehyde, pyruvic acid, and metamidodimethylaniline for two hours. It is deposited from alcohol in minute, reddish-yellow needles melting at 275°. The *silver* salt is anhydrous, the *lead* and *copper* salts each contain 1 mol. H<sub>2</sub>O, and the *zinc* salt 2½ mols. H<sub>2</sub>O. On distillation, the acid yields *2-dimethylamido-2'-phenylquinoline*, NMe<sub>2</sub>·C<sub>9</sub>NH<sub>5</sub>Ph, the *platinochloride*, *dichromate*, and *picrate* of which have been analysed; the last named melts at 180°. M. O. F.

**Synthesis of Isoquinoline.** By C. GOLDSCHMIDT (*Ber.*, 1894, **27**, 2795).—The preparation of isoquinoline from cinnamalaldoxime has been recently described (Abstr., 1894, i, 552), the yield being 2 per cent.; if the aldoxime is heated on the water bath with phosphoric anhydride and dry infusorial earth (3 parts), the yield is increased to 10 per cent. J. B. T.

**A Platonic Compound of Glyoxaline.** By L. BALBIANO (*Gazzetta*, 1894, **24**, ii, 101—104; compare Abstr., 1893, i, 674).—A double compound, (C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>PtCl<sub>4</sub>, of platonic chloride and glyoxaline is obtained on boiling glyoxaline with sodium platinochloride solution; it forms a microcrystalline, yellow powder, insoluble in nitro-hydro-

chloric acid and most other solvents. The same substance is obtained on heating glyoxaline platinochloride at 180—205°, but cannot be prepared by boiling an aqueous solution of the platinochloride; in the latter case a mixture of platinum with platinous chloride is deposited.

W. J. P.

**Methylglyoxalidine or Lysidine.** By A. LADENBURG (*Ber.*, 1894, **27**, 2952—2957).—Methylglyoxalidine was first prepared by A. W. Hofmann; an increased yield of purer substance is obtained by distilling ethylenediamine hydrochloride (1 mol.) with sodium acetate (2 mols.); it boils at 195—198°, and melts at 105°, not at 221—224° and 85° respectively, as Hofmann states. The *urate* crystallises in triclinic prisms;  $a : b : c = 0.48736 : 1 : 0.51207$ ; it is soluble in about 6 parts of water at 18°; lysidine itself is a specific for both chronic and acute gout. The *hydrogen tartrate*,  $C_4H_8N_2 \cdot C_4H_6O_6$ , crystallises in monoclinic prisms;  $a : b : c = 0.4588 : 1 : 0.2931$ ,  $\beta = 63^\circ 5'$ ; a full crystallographic description of both salts is given. The hydrochloride is crystalline and hygroscopic. The *mercurichloride*,



crystallises in colourless prisms. The *methyl-derivative*,  $C_5H_{10}N_2$ , is colourless and crystalline, and melts at 90°. The *hydrochloride* and *platinochloride* have also been prepared; the former is crystalline.

J. B. T.

**Preparation of Thiouvinuric acid (Amidothiazolecarboxylic acid).** By C. BOETTINGER (*Arch. Pharm.*, 1894, **232**, 349—351).—Amidothiazolecarboxylic acid hydrobromide is prepared by intimately mixing tribromopyruvic acid (3 parts) with thiocarbamide (2 parts) at ordinary temperatures, the violence of the action being moderated by the addition of a little absolute alcohol. The product is dissolved in alcohol, evaporated to dryness, the residue treated successively with carbon bisulphide and cold water, and the acid purified by recrystallisation from hot water.

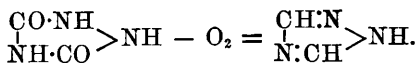
J. B. T.

**Urazoles and Triazoles.** By G. PELLIZZARI and G. CUNEO (*Gazzetta*, 1894, **24**, i, 499—511).—Hydrazodicarbonamide may be prepared by heating a mixture of carbamide and a salt of hydrazine (compare Curtius and Heidenreich, *Abstr.*, 1894, i, 166). On heating the carbonamide at 180—250°, it evolves ammonia and yields *urazole*,  $\begin{array}{c} \text{CO} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{CO} \end{array} > \text{NH}$  or  $\begin{array}{c} \text{C(OH):N} \\ | \\ \text{N:C(OH)} \end{array} > \text{NH}$ ; it forms colourless crystals, melting and decomposing at 244°. It is soluble in water or alcohol, and crystallises unaltered from hydrochloric acid. It gives a red coloration with ferric chloride or sulphuric acid containing a little nitric acid, and reduces ammoniacal silver nitrate in the cold. Urazole decomposes carbonates and reddens litmus. The *ammonio-derivative*,  $C_2O_2N_3H_2 \cdot NH_4$ , is obtained in colourless crystals, and gives off ammonia at 100°. The *argento-compound* is an amorphous, white powder, whilst the *barium-derivative* forms colourless, transparent crystals containing  $3H_2O$ . The *triplobic-derivative*,  $C_2O_2N_3Pb_3$ , is obtained

as a white precipitate, and most of the compounds with the other heavy metals are insoluble in water.

On heating an anhydrous mixture of biuret with a hydrazine salt at 150—160°, ammonia is evolved and urazole is formed together with a little hydrazodicarbonamide; a 97 per cent. yield of the latter substance is obtained if carbamide is used in place of biuret.

Triazole (compare Blodin, Abstr., 1892, 735) may be prepared by heating urazole with phosphorous pentasulphide at 180—200°.



W. J. P.

**Oxidation of Formazyl Compounds.** By H. v. PECHMANN and P. RUNGE (*Ber.*, 1894, **27**, 2920—2930; compare Abstr., 1894, i, 240).—When ethylic formazylformate is oxidised by means of amyl nitrite and hydrochloric acid in alcoholic solution, it is converted into *ethylic diphenyltetrazoliumcarboxylate chloride*,  $\text{COOEt}\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{NPh} \\ | \\ \text{N}\cdot\text{NPhCl} \end{array}$ , which crystallises with 1 mol. alcohol in colourless prisms, effloresces in the air, and melts and decomposes at 195—198°.

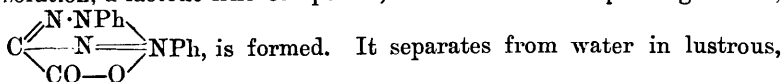
This reaction is characteristic of all the formazyl compounds. The free base corresponding with the chloride cannot be isolated pure, but probably has the formula  $\text{COOEt}\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{NPh} \\ | \\ \text{N}\cdot\text{NPh}\cdot\text{OH} \end{array}$ , being formed from the direct product of oxidation by intramolecular change, the hydroxyl group passing from one nitrogen atom to the other. The formula ascribed to these compounds is confirmed by the fact that when the chloride just described is submitted to dry distillation it yields nearly one-third of its weight of azobenzene. The oxidation products are all remarkably stable towards acids, but are easily reduced by alkaline reducing agents to the original formazyl compounds. The aqueous solutions of the free bases have an alkaline reaction and absorb carbonic anhydride from the air, but only yield red resinous substances on evaporation. The salts, on the other hand, crystallise well, and form neutral solutions in water.

Ethylic diphenyltetrazoliumcarboxylate chloride is very readily soluble in water and gives crystalline precipitates of the *bromide*, *nitrate*, *nitrite*, *iodide*, *chromate*, and *phosphate*, when the corresponding sodium or potassium salts are added to its solution. Zinc-dust reduces it to ethylic formazylformate, whilst alkaline reducing agents form a salt of the free acid. Subcutaneous injections of the chloride produces sickness and affect the circulation, death being finally brought about from paralysis of the heart.

*Diphenyltetrazoliumcarboxylic acid chloride*,  $\text{COOH}\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{NPh} \\ | \\ \text{N}\cdot\text{NPhCl} \end{array}$ , may be obtained by the hydrolysis of the ethylic salt just described, or by the oxidation of formazylformic acid. It forms long, colourless needles, melts and decomposes at 256—257°, and is only sparingly soluble in water. The *nitrate* crystallises in lustrous tablets and melts at 207°.



When the free acid is boiled with water or with sodium carbonate solution, a lactone-like compound, which is the corresponding *betaine*,



twinned crystals, and melts at 161°. Dilute acids dissolve it with formation of the corresponding salts of diphenyltetrazoliumcarboxylic acid hydroxide. When it is heated, azobenzene is produced. This formation of an anhydro-compound is an additional confirmation of the formula ascribed to this series of compounds.

*Diphenyltetrazolium chloride*,  $\text{HC} \begin{array}{c} \text{N} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} : \text{NPhCl} \end{array}$ , may be obtained by the oxidation of formazylhydride or by boiling the chloride of the carboxylic acid just described with alcohol, or heating it or its ethylic salt with hydrochloric acid at 160–180°. It crystallises in stellate groups of lustrous needles, and melts and decomposes at 268°. The *platinochloride* forms orange-yellow prisms, the *aurochloride* melts at 209°, and the *iodide* at 237°.

*Triphenyltetrazolium chloride*,  $\text{PhC} \begin{array}{c} \text{N} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} : \text{NPhCl} \end{array}$ , is prepared from formazylbenzene, and crystallises in lustrous needles which melt and decompose at 243°. The *platinochloride* melts at 237°, the *bromide* at 255°.

*Diphenylparatolyltetrazolium chloride*,  $\text{PhC} \begin{array}{c} \text{N} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} : \text{NCl} \cdot \text{C}_6\text{H}_4 \end{array}$ , is obtained from *h*-phenyl- $\alpha$ -paratolylformazylbenzene, and melts at 229°.

*Benzeneazodiphenyltetrazolium chloride*,  $\text{PhN} \cdot \text{N} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{N} : \text{NPhCl} \end{array}$ , from benzeneazoformazylbenzene, crystallises in brownish-yellow prisms with a violet iridescence, and melts and decomposes at 249°. The solution of the base is yellowish-brown. A. H.

**Constitution of the Additive Compounds of the Cinchona Alkaloids with Ethylic Iodide.** By Z. H. SKRAUP (*Monatsh.*, 1894, 15, 433–436).—The author has examined the action of oxidising agents on the additive compounds of ethylic iodide with the cinchona alkaloids in the expectation that the pyridine ring of the so-called “first half” would be opened. The results obtained in the case of cinchonine ethiodide have not confirmed this supposition, but are of interest, inasmuch as they confirm the author’s previous supposition that the ethyl group combines with the nitrogen atom of the quinoline ring of the “second half” of the molecule.

The hydriodide of cinchonine ethiodide was treated with the requisite quantity of silver nitrate to remove the hydrogen iodide, potassium permanganate gradually added to the resulting aqueous solution in the cold, and the product, after filtering from manganese dioxide, was precipitated successively with lead acetate, mercuric chloride, and cadmium chloride. From the first two precipitates, no crystalline products could be obtained, but from the last a substance was separated, crystallising from water in pointed prisms of the colour of

chromium trioxide. It melts and decomposes at about  $200^{\circ}$ , and has the composition  $C_{12}H_{12}NO_2I + H_2O$ , the water of crystallisation being readily given off. From its composition and properties, it appears probable that it is an additive compound of cinchonic acid and ethylic iodide, and this has been confirmed by its direct formation from these two substances. It follows, therefore, that in the original cinchonine ethiodide the ethyl group is in combination with the nitrogen atom of the quinoline group of the second half of the alkaloid molecule.

When cinchonic acid ethiodide is treated with silver chloride, it is converted into the corresponding *ethochloride*, which crystallises in colourless prisms and melts at  $229^{\circ}$ . H. G. C.

**Action of Water on Trihydriodocinchonine.** By G. PUM (*Monatsh.*, 1894, **15**, 446—452).—The author has previously shown (Abstr., 1893, i, 180) that trihydriodocinchonine is converted by alcoholic potash into cinchonine and isocinchonine, and by silver nitrate into  $\beta$ -cinchonine and isocinchonine, whilst Lippmann and Fleissner (Abstr., 1893, i, 736), by heating the same compound with water at  $150$ — $160^{\circ}$  in a sealed tube, obtained cinchonine, isocinchonine, and a new base, allocinchonine. The author has therefore examined the action of water at the ordinary pressure on trihydriodocinchonine, and finds that it is slowly but completely decomposed with formation of cinchonine and isocinchonine as the sole products. He has also repeated the experiments of Lippmann and Fleissner, but, in this case also, was unable to obtain any allocinchonine. This difference in the results may possibly be due to the presence of the allocinchonine as an impurity in the original cinchonine employed by Lippmann and Fleissner, or to some slight variation in the conditions under which the reaction was carried out. H. G. C.

**Technical Preparation of Cocaine from its Associated Alkaloids.** By A. EINHORN (*Ber.*, 1894, **27**, 2960).—A polemical reply to Liebermann (compare Abstr., 1894, i, 557). A patent has been granted for the author's method of synthesising cocaine, and the process is employed technically. J. B. T.

**Carnic acid.** By M. SIEGFRIED (*Ber.*, 1894, **27**, 2762—2763).—Carnic acid ("Fleischsäure"),  $C_{10}H_{15}N_3O_5$ , is contained in muscle as a compound of phosphoric acid, phosphocarnic acid, and forms readily soluble salts of calcium and barium, which decompose when their solutions are boiled, the corresponding phosphate being deposited. It forms a ferric compound, *carniferrin*, which is soluble in alkalis, and only gives the reactions for iron after being in contact with the reagents for some time. Carnic acid is monobasic, and yields crystalline salts of *zinc*, *copper*, and *barium*. The *silver* salt,  $C_{10}H_{13}N_3O_5Ag_2 + 2H_2O$ , is sparingly soluble; the second atom of silver probably replaces the hydrogen atom of an imido-group. Carnic acid also unites with 1 mol. of hydrogen chloride; the substance formed reacts with silver nitrate only on heating.

From its properties, carnic acid appears to be identical with anti-peptone, and has been observed among the products of tryptic digestion. A. H.

## Organic Chemistry.

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**Liquid Ethane and Propane.** By A. HAINLEN (*Annalen*, 1894, **282**, 229—245).—A detailed account of the experiments of which the results have already been published by L. Meyer (this vol., i, 1). A. H.

**Preparation of the Paraffins.** By F. KLUGE (*Annalen*, 1894, **282**, 214—228).—A detailed account of the experiments of which the results have already been published by L. Meyer (this vol., i, 2). A. H.

**Formation of Dicarbon Compounds from Carbon Bisulphide at Low Temperatures.** By V. MEYER (*Ber.*, 1894, **27**, 3160—3161).—When carbon bisulphide is chlorinated at 20—40°, the carbon tetrachloride formed is found to contain perchlorethylene and perchlorethane. M. O. F.

**New Class of Compounds of the Inactive Hydrocarbons.** By J. A. WANKLYN and W. J. COOPER (*Chem. News*, 1894, **70**, 211—212).—The authors find that hydrocarbons from Russian kerosene produce a reduction in temperature when mixed with acetic acid, and regard it as indicating combination, and, moreover, the products begin to distil at a lower temperature than would be the case if they were only mixtures of their components. D. A. L.

**Ferric Thiocyanate.** By L. ANDREWS (*Chem. News*, 1894, **70**, 165—166).—Spectroscopic examination of solutions of ferric thiocyanate in amyl alcohol distilled from phosphoric acid, and in absolute ethylic alcohol, show that the absorbent power of such solutions diminishes more rapidly than the concentration; and inasmuch as the molecular conductivity of such solutions is found to diminish, with increasing dilution, in about the same ratio as the reciprocal of the absorption coefficient, the falling off of the colour cannot be due to electrolytic dissociation; and, as hydrolysis is out of the question in the present case, neither Magnanini's nor Ostwald's theory seems capable of fully explaining the behaviour of ferric thiocyanate in solution. Compared with aqueous solutions, a solution containing 0.0625 milligram of ferric thiocyanate per c.c. of amyl alcohol transmitted 42 per cent. of light of wave-length 587, about the same amount as an aqueous solution containing 0.247 milligram per c.c. D. A. L.

**Linalol and Licareol.** By P. BARBIER (*Bull. Soc. Chim.*, 1894, [3], **11**, 261).—Referring to Bouchardat's paper (*Abstr.*, 1893, i, 544), the author claims priority of discovery (*Abstr.*, 1892, 1236) of the tendency of acetic anhydride to cause the conversion of the alcohols

of this class into isomerides. He also denies the identity of linalol and licareol.

L. T. T.

**Constitution of Rhodinol from Oil of Pelargonium.** By P. BARBIER and L. BOUVEAULT (*Compt. rend.*, 1894, **119**, 334—337).—The principal constituent of oil of pelargonium is a somewhat oily liquid with a strong odour of roses; it boils at 115—116° under a pressure of 10 mm.; sp. gr. at 0° = 0.8866; rotatory power of a column 20 cm. long  $-12^{\circ} 28'$ . When heated at 150—160° with a large excess of acetic anhydride, it yields (together with a small quantity of a hydrocarbon which boils at 60—80° under a pressure of 10 mm.) an acetate which boils at 120° under a pressure of 10 mm., and has a somewhat agreeable odour; sp. gr. at 0° = 0.9158. This acetate combines with one molecular proportion of bromine. When hydrolysed, the liberated alcohol has its original boiling point, but its odour has become weaker, the sp. gr. has fallen to 0.8825, and the rotatory power of a column 200 mm. long has fallen to  $-7^{\circ} 12'$ . Phenyl isocyanate acts on the alcohol as a dehydrating agent, and yields only diphenylcarbamide.

This rhodinol from pelargonium is a primary alcohol, and when carefully oxidised yields an aldehyde containing the same number of carbon atoms. The yield is, however, somewhat small, a large quantity of condensation products of high boiling point being formed at the same time. The aldehyde has a mixed odour of peppermint and lemon, and boils at 105—108°, but cannot be separated from the excess of alcohol that always accompanies it. It yields a liquid oxime boiling at 140—150°, and this is converted by acetic anhydride into a nitrile,  $C_{10}H_{15}N$ , which boils at 112—113° under a pressure of 11 mm., and combines with one molecular proportion of bromine. The aldehyde has the composition  $C_{10}H_{16}O$ .

The products of the oxidation of rhodinol contain an acid,  $C_{10}H_{16}O_2$ , which boils at 149—150° under a pressure of 10 mm., and combines with one molecular proportion of bromine. More energetic oxidation yields acetone and an acid,  $C_7H_{12}O_4$ , which boils without decomposing above 300° under the ordinary pressure and at 250° under a pressure of 10 mm. It is a bibasic acid, and does not combine with bromine; when boiled with aniline, it yields an anilide which crystallises in slender, colourless needles melting at 206—207°, somewhat soluble in alcohol, especially on heating, but only slightly soluble in ether. When boiled with acetic anhydride, the acid yields a very viscous anhydride,  $C_7H_{10}O_3$ , which boils at 180° in a vacuum. This new bibasic acid is  *$\alpha$ -methyladipic acid*; attempts to prepare it synthetically were unsuccessful.

The rhodinol of oil of pelargonium differs from its isomerides, lemonol (geraniol) and licarhodol, with which it has hitherto been confounded, in that it does not readily lose water with formation of a terpene, and is not attacked by hydrochloric acid in the cold. Moreover, the hydrochloride, when heated with potassium acetate, yields rhodinol acetate, whereas the hydrochlorides of its isomerides yield a terpene. It is a primary alcohol with a ring-constitution, but with only one ethylenic function.

C. H. B.

**Syntheses in the Sugar Group.** By E. FISCHER (*Ber.*, 1894, 27, 3189—3232).—This paper is a compilation of the work accomplished by the author and his collaborators, together with the more important researches of other chemists in the same domain since the year 1891. It thus forms a continuation of the paper on the same theme (*Abstr.*, 1890, 1223) which the author delivered as a lecture before the German Chemical Society. The first section deals with experimental methods, and in the next section the present aspect of the sugar group is discussed, the known aldoses and ketoses being tabulated together with the mono- and di-basic acids and polyhydric alcohols derived from them. The author then deals with the stereochemistry of the sugar group, and from this leads up to the configuration of the sugars and allied compounds. He then describes a nomenclature which expresses the configuration of these compounds in a more concise manner, thus glucose is denoted "*hexose* + — + + " or "*hexapentolal* + — + +." These formulæ do not, however, represent, as did those of van't Hoff, the influence of a single asymmetrical carbon atom on the optical properties of the molecule, but only the position of one substituent to the right or left side of the configuration formulæ (compare *Abstr.*, 1891, 1173 and 1444). The last two sections are under the following headings: "Influence of Configuration on Chemical and Physical Properties" and "Importance of Stereochemical Results in regard to Physiology." The papers quoted have all appeared in this Journal, principally as abstracts; their collation has, however, enabled the author to draw some most important and suggestive deductions. A. R. L.

**Amount of Magnesia and Lime in Sugar Juice.** By J. WEISSBERG (*Bied. Centr.*, 1894, 23, 715; from *Oester.-Ungar. Zeits. Zuckerind. u. Landw.*, 22, 153—155).—Ignited magnesia is about 300 times less soluble in 10 per cent. sugar solution than lime, and is less soluble in boiling sugar solutions than in cold solutions. Inasmuch as magnesia is so sparingly soluble in pure sugar solutions, and much more soluble in sugar-lime solutions, it was thought possible to prepare a magnesia sucrate, or, at least, a lime-magnesia sucrate; neither compound could, however, be obtained. Beetroot juice (100 c.c.) was treated with milk of lime in the usual manner with addition of ignited magnesia (1 gram). After the first saturation, a few c.c. of milk of lime and some milk of magnesia were added to the juice, which was then saturated a second time. The filtered solution yielded an ash containing CaO, 0.351 gram; MgO, 0.021 gram; or about 17 times as much lime as magnesia.

Limestone containing 2 or 3 per cent. of magnesium carbonate would, therefore, have no appreciably injurious effect on the composition of the products, since magnesia is so slightly soluble in sugar juice. N. H. J. M.

**Iodide of Starch Reaction.** By C. MEINEKE (*Chem. Zeit.*, 1894, 18, 157—160).—An aqueous solution of iodine may be added to a solution of starch until the liquid is decidedly yellowish, without developing any blue colour. The smallest amount of potassium iodide,

however, is sufficient to give the reaction. This seems at first a confirmation of Mylius's statement, that iodide of starch contains potassium or hydrogen iodide as an essential constituent; but the author's investigation proves that the presence of a soluble iodide is not at all necessary for obtaining the blue compound. The author has tabulated the results of a large number of experiments, showing that the compound is also formed, more or less completely, in the presence of other salts such as potassium, sodium, ammonium, calcium, and barium chloride; potassium, sodium, ammonium, and magnesium sulphate; potassium alum; potassium and sodium baborate.

L. DE K.

**Maltol.** By H. KILIANI and M. BAZLEN (*Ber.*, 1894, 27, 3115—3120; compare J. Brand, *Abstr.*, 1894, i, 270).—Maltol forms characteristic metallic salts. The *zinc* salt separates in colourless needles which retain water; the *copper* salt is anhydrous. The *calcium* salt crystallises in silky needles containing  $5\text{H}_2\text{O}$ ; it becomes yellow in contact with air or in a vacuum, owing to loss of water. The *lead*, *barium*, *cadmium*, *potassium*, and *ammonium* salts are also crystalline. *Benzoylmaltol*,  $\text{C}_6\text{H}_5\text{O}_2\cdot\text{OBz}$ , is colourless and neutral; it melts at  $115-116^\circ$ .

Oxidation of maltol with potassium permanganate gives rise solely to acetic acid and carbonic anhydride, the same products being formed on treating the aqueous solution with silver oxide. Maltol is not acted on by hydriodic or sulphuric acids, and no change occurs when the solution in alcohol or acetic acid is saturated with hydrogen chloride. Bromine has no action on maltol dissolved in chloroform, but the aqueous solution yields a syrupy acid which loses bromine very readily.

It is clear from these observations that the constitutional formula suggested for maltol (*loc. cit.*) must be considerably modified, and the authors prefer to regard it as a methylpyromeconic acid.

M. O. F.

#### **Nitrogenous Compound prepared from "Fungus-cellulose."**

By E. WINTERSTEIN (*Ber.*, 1894, 27, 3113—3115; compare *Abstr.*, 1894, ii, 425).—The author has already shown that the cellulose obtained from various fungi contains a considerable quantity of nitrogenous constituents which are not of a proteid nature. Further investigation has shown that when the fungus-cellulose is heated with hydrochloric acid, it yields glucosamine hydrochloride, identical with the product obtained in a similar manner from chitine (*Abstr.*, 1885, 53; 1886, 329). Whether the constituent which gives rise to the formation of glucosamine is identical with chitine has not yet been ascertained.

H. G. C.

**Action of Halogen Hydracids on Formaldehyde in presence of Alcohols.** By L. HENRY (*Compt. rend.*, 1894, 119, 425—426).—The reaction recently described by Favre (this vol., i, 14) was previously observed by the author (*Bull. Acad. Sci. Belge*, [3], 25, 439), and also by P. Henry (*Abstr.*, 1892, 27); the former investigated the action of hydrobromic and hydriodic acids as well as that of hydrochloric acid.

C. H. B.

**Chloro-formoxime.** By R. SCHOLL (*Ber.*, 1894, **27**, 2816—2822).—This substance, which has recently been described by Nef (this vol., i, 10), was obtained by the author in 1892, having been regarded as the dihydrochloride of fulminic acid. The observations of Nef are fully confirmed. M. O. F.

**Cause of the Transformation of Ethylic  $\alpha$ -Bromacetoacetate into Ethylic  $\gamma$ -Bromacetoacetate.** By A. HANTZSCH (*Ber.*, 1894, **27**, 3168—3169; compare *Abstr.*, 1894, i, 227).—This remarkable intra-molecular change is due to the agency of traces of hydrogen bromide, and is checked by the presence of moisture. M. O. F.

**Free Acids from Beeswax.** By T. MARIE (*Compt. rend.*, 1894, **119**, 428—431).—The free acid present in beeswax was regarded by Brodie as a single substance; but Schalfesew and Nafzger have shown that it is a mixture. The author finds that the separation of the acids cannot readily be effected by Heintz's method of fractional precipitation with metallic acetates, but is easily attained by means of fractional crystallisation from methylic alcohol, provided all organic substances except the acids are first removed.

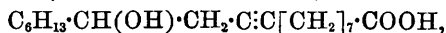
The wax is extracted with boiling methylic alcohol, and, after the greater part of the solvent has been distilled off, the cooled and crystallised residue is pressed in order to remove the oleic compounds and the colouring matters. The cake is melted, washed several times with boiling water, decolorised with charcoal, and filtered through paper; it is, then heated with lime and potash-lime until evolution of hydrogen ceases, in order to destroy myricin. The powdered mass is next suspended in water, heated to boiling, and saturated with dilute hydrochloric acid, the calcium salts which precipitate being collected, washed, dried, and treated with boiling alcohol and benzene to remove neutral substances. The acids are then liberated, and, after crystallisation from methylic alcohol, melt at 79—80°.

The mixture of acids is well triturated with 30 times its weight of methylic alcohol, heated carefully to boiling, and filtered at 60°. The filtrate contains chiefly cerotic acid, which crystallises on cooling. This treatment is repeated with successively diminishing volumes of alcohol until the residue melts at 78°. The dissolved product will then melt at 76°. A single crystallisation from ethylic alcohol raises this melting point to 77·5°.

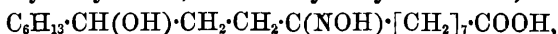
Crude cerotic acid has been described as a single substance, but in reality it contains from 30 to 40 per cent. of analogous acids. The author is investigating the properties of the pure acids and its salts.

C. H. B.

**Constitution of Ricinoleic and Ricinostearolic acids.** By A. G. GOLDSOBER (*Ber.*, 1894, **27**, 3121—3129; compare J. Baruch, *Abstr.*, 1894, i, 170).—Ricinostearolic acid,



when treated with concentrated sulphuric acid, yields ketohydroxystearic acid,  $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{COOH}$ . The latter gives with hydroxylamine, ketoximehydroxystearic acid,

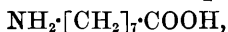


and this acid is converted by phosphorus pentachloride into an oil, which, when heated with fuming hydrochloric acid at 180—200°, yields  $\gamma$ -decalactone,  $\text{CH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{CO} > \text{O}$ , amidocaprylic acid,  $\alpha$ -hexyltrimethylenimine,  $\text{C}_6\text{H}_{13}\text{CH} < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} > \text{CH}_2$ , and azelaic acid.

*Ketohydroxystearic acid* forms silky crystals, and melts at 84—85°. The *barium* and *silver* salts are colourless, and the *ethylic* salt melts at 54·5°; the *acetyl* derivative is a yellow oil. The *phenylhydrazide* is formed when the acid is heated with phenylhydrazine at 150°.

*Ketoaimethydroxystearic acid* is an oil which is decomposed into hydroxylamine and ketoxystearic acid by dilute mineral acids. On heating it with alcoholic ammonia and adding hydrochloric acid, the product exhibits the characteristic reaction of pyrroline derivatives.

The *hydrochloride* of  $\alpha$ -hexyltrimethylenimine is hygroscopic, and yields the yellow *platinochloride*. *Amidocaprylic acid*,



melts at 172°, and its *hydrochloride* at 147°.

M. O. F.

**Turkey-red Oil.** By P. JULLIARD (*Bull. Soc. Chim.*, 1894, [3], 11, 280—286).—This is a continuation of the author's previous work (*Abstr.*, 1892, 819, and 1893, i, 455) on the action of sulphuric acid on castor-oil and on ricinoleic acid. *Diricinic acid*,  $\text{O}(\text{C}_{17}\text{H}_{32}\text{COOH})_2$ , is a bibasic acid. It is a thick, oily liquid, soluble in alcohol in all proportions, whilst its *ethylic* and *methylic* salts are but sparingly soluble in alcohol. *Ricinoricinic acid*,  $\text{OH}\cdot\text{C}_{17}\text{H}_{32}\text{CO}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\text{COOH}$ , best prepared by heating ricinoleic acid at 170—180°, is the first member of the series of polymerides of ricinoleic acid, and is a monobasic acid. *Dihydroxystearosulphuric acid*,  $\text{SO}_4\text{H}\cdot\text{C}_{17}\text{H}_{33}(\text{OH})\cdot\text{COOH}$ , closely resembles ricinosulphuric acid in properties. *Dihydroxystearic acid*,  $\text{C}_{18}\text{H}_{36}\text{O}_4$ , is very soluble in alcohol and ether, sparingly in light petroleum, and melts at 66—68°. A solid acid,  $\text{C}_{36}\text{H}_{70}\text{O}_7$ , was obtained, melting at 70—73°, which appears to be a molecular compound of dihydroxystearic acid with ricinoleic acid. *Isoricinoleic acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_3$ , is an oily liquid, soluble in alcohol and in light petroleum, and appears to be a ketonic acid.

L. T. T.

**Action of Thionyl Chloride on Organic Acids and Aldoximes.** By C. MOUREU (*Compt. rend.*, 1894, 119, 337—340).—See this vol., ii, 43.

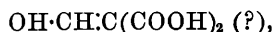
**Preparation of Thiodiglycollic acid.** By J. M. LOVÉN (*Ber.*, 1894, 27, 3059—3060).—An improved method of preparation. 95 grams of crystallised chloracetic acid is placed in a large beaker, and a solution, heated to 35°, of 145 grams of crystallised sodium carbonate in 50 c.c. of water is added. 45 grams of sodium hydroxide is dissolved in water, so that the solution has a volume of 100 c.c., one half is saturated with hydrogen sulphide, and then the two halves are added simultaneously to the solution in the beaker, which is meanwhile shaken or stirred. The pasty mass is allowed to stand



for three hours; 110 grams of strong sulphuric acid is then added, carefully, but without cooling, and the hot solution is filtered, and allowed to cool. After six hours, the crystals of crude thiodiglycollic acid are collected and dried; they weigh about 70 grams, and contain 10—15 per cent. of sodium hydrogen sulphate. The crude crystals are dissolved in hot water (50 c.c. for every 70 grams), and the solution is filtered; on cooling, 53 grams of very pure thiodiglycollic acid is deposited.

The mother liquor from the crude crystals, evaporated until it weighs 270 grams, is cooled to 40°, and then filtered. The filtrate, on further cooling, yields crystals of thiodiglycollic acid; these are purified by recrystallisation from the mother liquor of the first crop of pure crystals, and then weigh 10 grams. 63 grams of the pure acid are thus obtained from 95 grams of chloracetic acid, a yield which is 84 per cent. of the theoretical. C. F. B.

**Hydrolysis of Ethylic Dicarboxyglutaconate.** By H. W. BOLAM (*Ber.*, 1894, **27**, 3061—3062).—When ethylic dicarboxyglutaconate (1 mol.) is boiled with 10 per cent. aqueous barium hydroxide (4 mols.), it is partly hydrolysed, malonic and another acid,



being formed. The barium salt of the latter acid resembles that prepared by Ruhemann and Morell (*Trans.*, 1891, 749) from ethylic amidoethylenedicarboxylate. C. F. B.

**Leucine from Pancreatic Digestion.** By R. COHN (*Zeit. physiol. Chem.*, 1894, **20**, 203—209).—The present research brings forward evidence to show that the leucine obtained in a pancreatic digestion of proteid matter is not a single substance, but a mixture of several isomeric substances. W. D. H.

**Derivatives of Dimethylalloxan.** By W. TECHOW (*Ber.*, 1894, **27**, 3082—3089).—*Dimethyldialuric acid*,  $\text{CO} < \begin{smallmatrix} \text{NMe}\cdot\text{CO} \\ \text{NMe}\cdot\text{CO} \end{smallmatrix} > \text{CH}\cdot\text{OH}$ , is best obtained by the action of sodium amalgam on a thick magma of amalic acid (tetramethylalloxantin) and water, the whole being well shaken and cooled. The product is poured into hot dilute hydrochloric acid, and filtered, the whole series of reactions being carried out quickly, as the acid is very soon reddened by the air, especially when moist. The acid forms compact prisms, reddens at 100°, melts and decomposes at 170°, and reduces silver and copper solutions in the cold. The *potassium* salt,  $\text{C}_6\text{H}_7\text{N}_2\text{O}_4\text{K}$ , forms voluminous flakes, which soon assume a deep blue colour in the air, and the *barium* salt,  $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_8\text{Ba} + 2\text{H}_2\text{O}$ , forms microscopic crystals.

*Dichlorodimethylbarbituric acid*,  $\text{CO}:(\text{NMe}\cdot\text{CO})_2\cdot\text{CCl}_2$ , is readily obtained by the action of phosphorus pentachloride on amalic acid at 180°; it crystallises from alcohol in delicate, white needles or well-developed prisms, melts at 157° (uncorr.), and on long continued boiling with water loses hydrogen chloride, with formation of dimethylalloxan. When treated with sodium amalgam, it is con-

verted into the dimethylbarbituric acid, already described by Mulder (Abstr., 1879, 618). *Dimethylvioluric acid*,  $\text{CO}:(\text{NMe}\cdot\text{CO})_2\cdot\text{C}\cdot\text{N}\cdot\text{OH}$ , is prepared by the action of hydroxylamine hydrochloride on dimethylalloxan, and forms hard, well-developed crystals melting at  $124^\circ$ . It is strongly acid, liberating carbonic anhydride from carbonates. The *potassium salt*,  $\text{C}_6\text{H}_6\text{N}_3\text{O}_4\text{K}$ , forms a deep bluish-violet, flocculent, crystalline mass, the *ammonium salt*,  $\text{C}_6\text{H}_6\text{N}_3\text{O}_4\text{NH}_4 + \text{H}_2\text{O}$ , deep red crystals, which change to pale red on heating, and the *barium salt*,  $\text{C}_{12}\text{H}_{12}\text{N}_6\text{O}_8\text{Ba} + \text{H}_2\text{O}$ , a heavy, red precipitate. When added in small quantities to hot concentrated nitric acid, it is converted into *dimethylnitrobarbituric acid*,  $\text{CO}:(\text{NMe}\cdot\text{CO})_2\cdot\text{CH}\cdot\text{NO}_2$ , which separates from acetone as a white, microcrystalline mass, melting at  $148^\circ$ ; the *sodium salt*,  $\text{C}_6\text{H}_6\text{N}_3\text{O}_6\text{Na} + 4\text{H}_2\text{O}$ , crystallises in slender, yellow prisms.

The *ammonium salt of dimethylthionuric acid*,



is obtained by saturating a concentrated solution of ammonia with sulphurous anhydride and warming with solid ammonium carbonate and dimethylalloxan, and separates, on cooling, in fascicular aggregates of slender, lustrous needles; the water of crystallisation is evolved at  $105^\circ$ , the salt simultaneously assuming a red colour, and, on further heating, it decomposes completely at  $180^\circ$ . On adding barium chloride to its solution, the *barium salt*,  $\text{C}_6\text{H}_7\text{N}_3\text{O}_6\text{SBa}$ , separates in silky crystals. The free acid is an amorphous mass, which is readily soluble in water, has strongly acid properties, and, on boiling in aqueous solution, is converted into sulphuric acid and *dimethyluramil*,  $\text{CO}:(\text{NMe}\cdot\text{CO})_2\cdot\text{CH}\cdot\text{NH}_2$ . The latter compound is also obtained by the reduction of dimethylvioluric acid or of dimethylnitrobarbituric acid, but is best prepared by boiling ammonium dimethylthionurate with fuming hydrochloric acid, diluting with water, and neutralising with ammonium carbonate. Dimethyluramil then separates in snow-white, silky flakes, which melt and decompose at about  $200^\circ$ , and, on exposure to the air in the moist condition, quickly become dark red. It reduces silver and copper solutions, is decomposed by alkalis, even by ammonium carbonate, but unites with acids to form unstable salts; the *hydrochloride* forms small, hard crystals, which lose hydrogen chloride in a vacuum, and the *platinochloride*,  $(\text{C}_6\text{H}_7\text{N}_3\text{O}_6)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in yellow prisms.

*Dimethylpseudouric acid*,  $\text{CO}:(\text{NMe}\cdot\text{CO})_2\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , is prepared by the action of a concentrated solution of potassium cyanate on dimethyluramil. It forms small, white crystals, reddens at  $100^\circ$ , melts and completely decomposes at  $210^\circ$ , and reduces silver solutions. The *potassium salt*,  $\text{C}_7\text{H}_5\text{N}_4\text{O}_4\text{K} + \text{H}_2\text{O}$ , is crystalline, and the *copper salt*,  $(\text{C}_7\text{H}_5\text{N}_4\text{O}_4)_2\text{Cu} + 2\text{H}_2\text{O}$ , is a pale green precipitate, which loses its water of crystallisation at  $105^\circ$ , the colour changing simultaneously to yellowish-brown.

H. G. C.

**Action of Iodine and Potassium Hydroxide on Uric Acid.** By E. BRYK (*Monatsh.*, 1894, 15, 519—529).—Kreidl has described a method for the estimation of uric acid by treating it with potassium

hydroxide and iodine, and subsequently titrating with thiosulphate (Abstr., 1893, ii, 558). The author finds that the action of iodine on a solution of uric acid, to which potassium hydroxide has been previously added, depends on the proportion in which the substances are present and also on the temperature. If only a small excess of potassium hydroxide is employed, say in the proportion of 2.25 mols. to 1.3 atoms of iodine and 1 mol. of uric acid, and the mixture is kept cool, a yellow insoluble substance separates. This on analysis gave the numbers C = 28.37—26.86, H = 4.39—3.71, N = 28.53—29.19, and on solution in potash or sulphuric acid and subsequent reprecipitation with water gave uric acid. When a similar mixture is warmed, potassium urate, carbonic anhydride, and ammonia are formed. The employment of a larger proportion of potassium hydroxide, say 4 mols. to 2 atoms of iodine and 1 mol. of uric acid, gives rise to allantoin and carbonic anhydride; the yield of the former is good (40—50 per cent.). G. T. M.

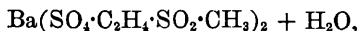
**Polymeric Ethoxysulphonethylenesulphinic Lactone.** By G. WALTER (*Ber.*, 1894, **27**, 3043—3045).—When an aqueous solution of free ethoxysulphonethylenesulphinic acid is evaporated to dryness, there is formed, in addition to the lactone soluble in water, already described (Abstr., 1893, i, 459), an insoluble polymeric modification, which has, however, the same melting point and chemical properties as the soluble variety. It can be converted into the latter by hydrolysing it with baryta water, liberating the free acid from the barium salt so obtained, and evaporating the solution of this acid. C. F. B.

**Some Derivatives of Ethoxymethylsulphone.** By G. WALTER (*Ber.*, 1894, **27**, 3045—3049; compare Abstr., 1893, i, 459).—Ethoxymethylsulphone,  $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_3$ , on treatment with phosphorus pentachloride, yields *chlorethylmethylsulphone*,



which melts at 8.5—9°. When this is treated with ammonia, there are formed, besides ammonium chloride, the hydrochlorides of *primary* and *secondary* methylsulphonethylamine,  $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_3$  and  $\text{NH}(\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_3)_2$ . The first hydrochloride forms deliquescent prisms, and the corresponding orange *platinochloride* melts and decomposes at 220—221°. The second hydrochloride melts at 202—203°, the orange *platinochloride* at 159—160°, and the *benzoyl-derivative* at 131°; the free base forms stable crystals.

If ethoxymethylsulphone is allowed to remain with cold, strong, sulphuric acid, and the mixture then added to a magma of water, ice, and barium carbonate, *barium methylsulphonethylene sulphate*,



is formed. This is readily hydrolysed, by boiling with water, yielding barium sulphate, sulphuric acid and ethoxymethylsulphone; ammonia converts it into the amines described above. C. F. B.

**Action of Sulphuric Acid on Bromothiophen.** By A. TÖHL and K. SCHULTZ (*Ber.*, 1894, **27**, 2834—2839; compare Abstr., 1894, i, 117 and 276).—In addition to the results already described (*loc. cit.*), it is found that slightly fuming sulphuric acid converts tribromothiophen into tetrabromothiophen, the sulphonic acids of dibromo- and tribromothiophen being also formed in small quantities. If fuming acid is employed, perbromodithienyl and tetrabromothiophen are formed. M. O. F.

**Synthesis of Metachlorotoluene and of Symmetrical Chloro-xylene from Ethylic Acetoacetate.** By A. KLAGES and E. KNOEVENAGEL (*Ber.*, 1894, **27**, 3019—3025; compare this vol., i, 48).—*Dihydrometachlorotoluene* [ $\text{Me}:\text{H}_2:\text{Cl} = 1:2:3:5$ ] is prepared by the action of phosphoric chloride on 3-methyl- $\Delta_2$ -keto-tetrahydrobenzene; the intermediate methyltrihydrodichlorobenzene could not be isolated, it is a highly refractive liquid with an aromatic odour, boils at  $78-80^\circ$  (25 mm.), at  $160-170^\circ$  under atmospheric pressure, and is volatile with steam, some of the compound being decomposed. The yield is 60 per cent. of the ketone employed. The ketone is regenerated by the action of sulphuric acid (95 per cent.), a tertiary alcohol being first formed which is either identical with the ketone or is converted into it by intramolecular rearrangement. The *dibromide* is unstable and could not be purified; on warming alone or with quinoline, hydrogen bromide is eliminated and metachlorotoluene is formed.

*2:3:5-Dihydrochloro-xylene* [ $\text{Me}:\text{Me} = 1:3$ ] is prepared in a similar manner to the toluene derivative from 3:5-dimethyl- $\Delta_2$ -keto-tetrahydrobenzene, which it closely resembles; it boils at  $78-80^\circ$  (15 mm.), and at  $176-178^\circ$  under ordinary pressures with little decomposition, darkens on exposure to air, and regenerates the ketone on treatment with sulphuric acid. The yield is 70 per cent. of the ketone employed.

The *dibromide* is unstable and is readily converted into *symmetrical chloro-xylene*, a highly refractive mobile liquid boiling at  $190-191^\circ$ ; its vapour rapidly attacks the skin. The *sulphonic acid* crystallises in lustrous plates, is readily soluble in water, and melts at  $65-68^\circ$ . The *sodium* and *barium* salts crystallise in plates. The *sulphonic chloride* and the *sulphonamide* crystallise in colourless needles melting at  $48-49^\circ$  and  $189-190^\circ$  respectively. The position of the sulphonic group has not been determined. J. B. T.

**Mercuric Phenoxides and Naphthoxides.** By E. DESESQUELLE (*Bull. Soc. Chim.*, 1894, [3], **11**, 263—269).—*Mercuric  $\beta$ -naphthoxide chloride*,  $\text{ClHg}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$ , obtained by shaking together aqueous solutions of mercuric chloride and potassium  $\beta$ -naphthoxide, crystallises in colourless prisms soluble in alcohol, insoluble in water. For medical purposes, the author proposes for this substance the name  *$\beta$ -sublimonaphthol*. *Mercuric  $\beta$ -naphthoxide*,  $\text{Hg}(\text{O}\cdot\text{C}_{10}\text{H}_7)_2$ , forms microscopic crystals, almost insoluble in the usual solvents but slightly soluble in boiling phenol. Acetic acid acts on it with development of heat, yielding *mercuric  $\beta$ -naphthoxide acetate* as a white, crystalline substance, soluble in alcohol, almost insoluble in water.

*Mercuric phenoxide chloride* forms colourless crystals melting about  $210^{\circ}$ , soluble in phenol or in a boiling alcoholic or aqueous solution of phenol. *Mercuric phenoxide hydroxide*,  $\text{OH}\cdot\text{Hg}\cdot\text{OPh}$ , is formed when a large excess of potassium phenoxide is employed, and crystallises in stellar groups of prisms. With acetic acid, this compound yields *mercuric phenoxide acetate*, crystallising in colourless prisms. The author has not been able to obtain the derivative  $\text{Hg}(\text{OPh})_2$ .

L. T. T.

**New Colour Reaction of Iridol.** By E. NICKEL (*Chem. Zeit.*, 1894, 18, 531).—When a solution of iridol (*Abstr.*, 1894, i, 48) in aqueous alcohol is warmed with a solution of mercuric chloride (2 parts) and sodium nitrite (1 part) in water (40 parts), a beautiful, violet coloration, having a bluish tinge, is developed. This reaction was previously described by the author as characteristic of vanillin, and, indeed, there is no essential difference between the colorations produced by the two substances.

A. R. L.

**Thioaniline (m.p.  $105^{\circ}$ ), and a new Isomeride.** By K. A. HOFMANN (*Ber.*, 1894, 27, 2807—2816).—The author has shown that Merz and Weith's thioaniline is orthodiamidophenylic sulphide,  $\text{S}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ ; orthodiamidophenylic bisulphide is also formed when aniline is heated with sulphur, and may be converted into orthodiamidophenylic sulphide by the addition of lead oxide to its solution in boiling aniline.

*Paradiamidophenylic sulphide* is prepared by heating a mixture of aniline, aniline hydrochloride, and sulphur for 6—7 hours at  $175^{\circ}$ ; it crystallises from boiling water in colourless, lustrous plates, which melt at  $85.5^{\circ}$ . The *hydrochloride* yields an emerald-green solution when heated with fuming sulphuric acid for half an hour at  $100^{\circ}$ . On adding lead peroxide to the solution in alcoholic hydrochloric acid, a green coloration is produced, changing to deep blue. The *benzoyl* derivative melts at  $234^{\circ}$ , and the *diacetyl* derivative at  $185^{\circ}$ ; the corresponding derivatives from orthodiamidophenylic sulphide melt at  $255^{\circ}$  and  $213$ — $215^{\circ}$  respectively.

*Paradiamidophenylic bisulphide*,  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2$ , is associated with the foregoing compound. It forms colourless needles, and melts at  $80^{\circ}$ ; the *diacetyl* derivative melts at  $205^{\circ}$ ; it yields paradiamidophenylic sulphide when strongly heated. The solution of the *hydrochloride* in alcohol is coloured deep cherry-red by lead peroxide, and the colourless solution in strong sulphuric acid becomes violet when heated. Sulphur is precipitated when hydrogen sulphide is passed through a solution of the hydrochloride in dilute hydrochloric acid, amidophenyl mercaptan remaining dissolved. When paradiamidophenylic bisulphide is diazotised, decomposed in alcoholic solution with copper powder, and saturated with hydrogen sulphide, thiophenol is produced, and parabromothiophenol is formed on displacing the amido-group with bromine.

M. O. F.

**Suggested Non-existence of Isopropyleneparamidophenol.** By A. MICHAELIS and K. LUXEMBOURG (*Ber.*, 1894, 27, 3005—3009).—Haegele's work on this compound has been repeated, and his

results are confirmed as regards its formation from pure acetone; it melts at 172—174°, is slowly hydrolysed by boiling with water, and more readily with dilute acids (compare Hantzsch and Freese, Abstr., 1894, i, 572, and this vol., i, 24). The calcium hypochlorite reaction is a delicate test for paramidophenol; the acetate reacts more readily than the hydrochloride; the dilute hypochlorite solution should be added gradually, as the violet colour is destroyed by excess of it.

J. B. T.

### Chlorides of Hydroxamic Acids and their Products of Change.

By A. WERNER (*Ber.*, 1894, 27, 2846—2850).—*Orthonitrobenzhydroxamic chloride*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CCl}\cdot\text{NOH}$ , is formed when dry chlorine is passed into a solution of orthonitrobenzaldoxime in chloroform; it melts at 92—94°. The *meta*-derivative melts at 94—95°, and the *para*-compound at 115—117°.

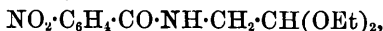
*Orthonitrobenzenylamidoxime*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$ , is obtained by warming the acid chloride with alcoholic ammonia. It forms bright yellow needles, which contain  $1\text{H}_2\text{O}$ ; the substance loses water at 80°, and melts at 141—142°. The *para*-derivative melts at 165—167°.

*Metadinitrobenziledioxime peroxide*,  $\begin{array}{c} \text{O}\cdot\text{N}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ | \\ \text{O}\cdot\text{N}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \end{array}$ , is produced when metanitrobenzhydroxamic chloride is warmed with concentrated aqueous potash. It melts at 183—185°. The *para*-compound melts at 197—198°.

*Orthonitrobenzenylpiperidoxime*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_5\text{NH}_{10})\cdot\text{NOH}$ , is obtained by mixing ethereal solutions of piperidine and orthonitrobenzhydroxamic chloride. It melts at 132—133°, and the *meta*-derivative melts at 159—160°. The *para*-compound melts at 166—167°.

M. O. F.

**Action of Amidoacetal on Orthonitrobenzoic Chloride and Paranitrobenzoic Chloride.** By W. LÖB (*Ber.*, 1894, 27, 3093—3097).—*Orthonitrobenzoylamidoacetal*,



is obtained in a manner analogous to the benzoyl derivative (Abstr., 1893, i, 300), and crystallises from ether on the addition of light petroleum in stellate groups of colourless needles melting at 70—71°. On treatment with cold fuming hydrochloric acid, it is converted into *orthonitrohippuraldehyde*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHO}$ , an amorphous, pale yellow substance, which softens at 90°, decomposes at a higher temperature, and reduces Fehling's solution. It could not be directly converted into the corresponding *orthonitrohippuric acid*, but the latter was obtained by the action of orthonitrobenzoic chloride and alkali on glycocine; it crystallises from hot water in long, narrow plates melting at 188°, and gives crystalline precipitates with silver and lead salts.

*Orthamidobenzoylamidoacetal*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , is prepared by the reduction of the nitro-compound with zinc dust and acetic acid in alcoholic solution, and crystallises from light petroleum containing a little ether, in druses of colourless needles, melting at

80—81°. By the action of concentrated hydrochloric acid, not only are both the ethyl groups eliminated, but also the elements of water, with formation of the *anhydride of orthamidohippuraldehyde*, a white, amorphous compound, which decomposes at 300° without previously melting; it has the empirical formula  $C_9H_5N_2O$ , but is probably a polymeride.

*Paranitrobenzoylamidoacetal* is prepared in a similar way to, and closely resembles the ortho-derivative; it melts at 82°, and, with hydrochloric acid, yields *paranitrohippuraldehyde*, which forms colourless, amorphous flakes, softens at 100°, and reduces Fehling's solution. Like the ortho-compound, it cannot be converted into the corresponding *acid*, which was prepared from paranitrobenzoic chloride and glycocine, and forms colourless prisms melting at 129°.

When paranitrobenzoylamidoacetal is treated with reducing agents, it does not, like the ortho-derivative, yield the amido-compound, but is converted into the azoxy- or azo-derivative according to the strength of the reducing agent employed. *Parazoxybenzoylamidoacetal*,  $ON_2[C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2]_2$ , is obtained by the action of zinc dust and acetic acid in the cold, and crystallises in pale red plates melting at 182°.

*Parazobenzoylamidoacetal*,  $N_2 \cdot [C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2]_2$ , is formed if the solution is boiled with zinc dust and acetic acid; it crystallises in long, narrow, carmine-red plates, melting at 202.5°.

H. G. C.

**Derivatives of Amidoaldehyde.** By H. HELLER (*Ber.*, 1894, **27**, 3097—3102).—E. Fischer has already shown that amidoacetal combines with aldehydes and acid chlorides, and that the products are resolved by the action of hydrochloric acid into the corresponding derivatives of amidoaldehyde. The author, in the present paper, describes a number of these derivatives.

*Paramethoxybenzylideneamidoacetal*,  $OMe \cdot C_6H_4 \cdot CH : N \cdot CH_2 \cdot CH(OEt)_2$ , is obtained by the action of amidoacetal on anisaldehyde, and forms a colourless oil having a bluish fluorescence, and boiling at 190° (corr.) under 12 mm. pressure. It yields salts, of which the *oxalate*, melting at 138°, is the most stable. On reduction with sodium in alcoholic solution, it yields *paramethoxybenzylamidoacetal*,



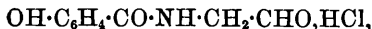
which is a colourless, slightly fluorescent liquid boiling at 187° (corr.) under 12 mm. pressure; its *oxalate* crystallises in colourless needles melting at 174°.

*Paramethoxybenzylamidoaldehyde*,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CH \cdot CHO$ , is obtained in the form of the *hydrochloride* by the action of hydrochloric acid on the foregoing compound at 50°; it crystallises with  $\frac{1}{2}H_2O$ , reduces Fehling's solution strongly, and with alkalis yields the free aldehyde, which is amorphous. The *phenylhydrazone hydrochloride* crystallises from alcohol in lustrous, colourless plates which become brown at 150°; it is converted by alkalis into the oily free *phenylhydrazone*.

*Anisylamidoacetal*,  $OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CH(OEt)_2$ , is prepared

by the action of anisic chloride on a cooled ethereal solution of amidoacetal, the *hydrochloride* separating out in lustrous, white plates which are converted into the free base by alkalis; the latter forms yellowish, prismatic needles melting at 60–61°. With hydrochloric acid, it yields *paramethoxyhippuraldehyde*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHO}$ , the *hydrochloride* of which separates out in colourless cube-shaped crystals melting at 128° with decomposition. The free aldehyde forms amorphous flakes and reduces Fehling's solution strongly. The *phenylhydrazone* crystallises in colourless needles, which soon become reddish, and on heating turn brown and then melt at 126°; the *oxime* crystallises in slender, white needles, and melts and decomposes at 163°. By the action of bromine, the aldehyde is converted into *metabromoparamethoxyhippuric acid*,  $\text{C}_{10}\text{H}_{10}\text{O}_4\text{NBr}$ , which forms slender, white needles and melts at 161–162°; its *silver salt* crystallises from hot water in stellate groups of needles. When strongly heated with concentrated hydrochloric acid, it is converted into metabromanisic acid.

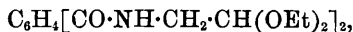
*Orthohydroxybenzylideneamidoacetal*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , obtained by the action of salicylaldehyde on amidoacetal, crystallises in yellow tablets melting at 32°, and boils at 188° (corr.) under 15 mm. pressure. *Orthohydroxybenzoylamidoacetal* is prepared by heating methylic salicylate with amidoacetal at 120°, and crystallises from light petroleum in yellowish, rhombic plates melting at 54°. By the action of strong hydrochloric acid, it is converted into the *hydrochloride* of *orthohydroxyhippuraldehyde*,



which forms white tablets, and melts at 150° with decomposition. The free aldehyde has only been obtained as a syrup with strongly reducing properties; its *phenylhydrazone* crystallises in pale yellow needles, and melts and decomposes at 134°; the *oxime* forms needles melting at 142°.

H. G. C.

**Phthalyl Compounds of Amidoacetal.** By W. ALEXANDER (*Ber.*, 1894, **27**, 3102–3105).—*Phthalyldiamidoacetal*,



is obtained by the action of phthalic chloride on amidoacetal in ethereal solution, and separates, on the addition of light petroleum, in colourless needles melting at 90°, and decomposing rather above 100°. The corresponding *aldehyde* is formed by the action on it of hydrochloric acid, the *hydrochloride* being thus obtained as a syrup which reduces Fehling's solution. By the action of alcoholic potash, phthalyl-diamidoacetal is converted into *orthobenzoylamidoacetalcarboxylic acid*,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , which separates on the addition of light petroleum to its ethereal solution in stellate groups of colourless needles containing  $1\text{H}_2\text{O}$ ; it melts and decomposes at about 100°.

*Terephthalyl-diamidoacetal* is prepared in a manner analogous to the phthalyl-derivative, and crystallises in flat needles or plates melting at 165°. The corresponding *aldehyde*,  $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHO})_2$ , is a bulky, white powder which only dissolves in concentrated hydro-



chloric acid and alkalis; its *phenylhydrazone* forms yellow flakes. *Terephthalaldiamidoacetic acid*,  $C_6H_4(CO \cdot NH \cdot CH_2 \cdot COOH)_2$ , is obtained by the action of bromine on the aldehyde, and crystallises from hot water in needles which melt at  $240^\circ$  with evolution of gas; the *silver* salt is a curdy precipitate which may be recrystallised from hot water, and the *copper* salt an insoluble, crystalline precipitate, which is blue when moist, but becomes green on drying. The acid may be more conveniently prepared by acting on glycocine with terephthalic chloride according to Baumann's method.

*Isophthalaldiamidoacetal*, obtained in the same manner as its isomerides, melts at  $75^\circ$ ; the corresponding *aldehyde* closely resembles the terephthalyl derivative, but cannot readily be converted into *isophthalaldiamidoacetic acid*, which was therefore obtained from glycocine and isophthalic chloride; it forms colourless cubes, and melts with decomposition at about  $210^\circ$ .  
H. G. C.

**Aromatic Nitro-derivatives.** By V. MEYER (*Ber.*, 1894, 27, 3153—3159).—Trinitrobenzoic chloride [ $COCl : (NO_2)_3 = 1 : 2 : 4 : 6$ ] is produced on heating trinitrobenzoic acid with a mixture of the oxychloride and pentachloride of phosphorus. It displays remarkable stability in presence of water, being only slightly decomposed when boiled with it for an hour (compare Sudborough, *Trans.*, 1894, 1030). The solution of trinitrobenzoic acid in alkali (1 mol.) is colourless, and yields a colourless silver salt with silver nitrate; but if excess of alkali is employed, a deep orange-red liquid is formed. On adding acid to this solution, unchanged trinitrobenzoic acid is thrown down; this behaviour is comparable with the development of a deep red coloration exhibited by trinitrobenzene in presence of alkali.

A small quantity of 1:3:5-dinitrobenzoic acid dissolved in dilute alkali forms a colourless solution, becoming deep violet when excess of strong alkali is added. After a few minutes, the liquid loses colour, and on remaining for two hours a further change occurs, and a stable, magenta coloration is developed.

The author criticises the conclusions drawn by Nef regarding the constitution of salts of the nitro-paraffins (this vol., i, 3).

M. O. F.

**Reduction of Paradimethylamidobenzoic acid and Paramidobenzoic acid.** By A. EINHORN and A. MEYENBERG (*Ber.*, 1894, 27, 2829—2834; compare *Abstr.*, 1894, i, 591).—*Paradimethylamido-hexahydrobenzoic acid*,  $C_6H_{10} \begin{smallmatrix} \text{CO} \\ \text{---} \\ \text{NHMe}_2 \end{smallmatrix} \text{O}$ , is obtained, in association with hexahydrobenzoic acid, by the reduction with sodium of paradimethylamidobenzoic acid dissolved in amyl alcohol. The acid liquefies at  $99$ — $100^\circ$ , resolidifies at  $130^\circ$ , and finally melts at  $218$ — $220^\circ$ ; it contains  $2\frac{1}{2}H_2O$ . It is a neutral substance, and forms a bright blue *copper* salt; the *platinochloride* melts at  $232^\circ$ .

*Paramido-hexahydrobenzoic acid*,  $C_6H_{10} \begin{smallmatrix} \text{CO} \\ \text{---} \\ \text{NH}_3 \end{smallmatrix} \text{O}$ , is formed on reducing with sodium paramidobenzoic acid dissolved in amyl alcohol, hexahydrobenzoic and valeric acids being formed simulta-

neously. On adding the aqueous solution to absolute alcohol, the acid crystallises in small, white plates which melt at 303—304°.

M. O. F.

**Isomeric Paramethylenedihydrobenzoic acids.** By A. EINHORN and R. WILLSTÄTER (*Ber.*, 1894, 27, 2823—2829; compare *Abstr.*, 1894, i, 523).—In addition to  $\Delta^{2,4}$ -paramethylenedihydrobenzoic acid, and the acid obtained by Einhorn and Friedländer on hydrolysing the methiodides of ethylic *r*-ecgonine and *l*-ecgonine, there exists a third acid,  $C_8H_8O_2$ , which remains liquid at  $-20^\circ$ . It is prepared by heating  $\Delta^{2,4}$ -paramethylenedihydrobenzoic acid with alcoholic potash for 48 hours in a reflux apparatus; it boils at  $160^\circ$  (20 mm.), and the *amide* melts at  $90^\circ$ . The crystalline acid (m. p. 55—56°) described by Einhorn and Friedländer is also formed when  $\Delta^{2,4}$ -paramethylenedihydrobenzoic acid is boiled with alcoholic potash for 12 hours; the *amide* melts at 101—102°. This acid and paramethylenedihydrobenzoic acid, on reduction, yield the same 1 : 4-ethylcyclopentanecarboxylic acid.

It is not yet clear whether the liquid acid just described is structurally different from the substance obtained by Einhorn and Friedländer, or whether the isomerism is geometrical in character.

M. O. F.

**Bismuth Salts.** By B. FISCHER and B. GRÜTZNER (*Arch. Pharm.*, 1894, 232, 460—466; compare *Abstr.*, 1894, i, 416).—The authors prepared basic bismuth salts by heating freshly precipitated bismuth hydroxide with the respective acids. *Basic bismuth paracresotate*,  $C_7H_7O \cdot COO \cdot BiO$ , and the *metacresotate* both form needles similar in all respects to the salicylate. No definite basic salts could be obtained from anisic, benzoic, or cinnamic acids. The *tartrate*,  $C_4H_4O_6 \cdot 2Bi(OH)_2$ , forms an amorphous, electrical, white powder. Attempts to prepare the basic nitrate by the action of the calculated quantity of a 5 per cent. alcoholic solution of nitric acid on freshly precipitated bismuth hydroxide were sometimes successful and sometimes not. The authors were unable to find out the conditions necessary to ensure a successful result.

L. T. T.

**Hydroxy-derivatives of Phenylbutyric acid.** By F. KOPISCH (*Ber.*, 1894, 27, 3109—3113).—In the course of their synthesis of phenyltetrose, Fischer and Stewart (*Abstr.*, 1892, 1447) obtained several hydroxy-derivatives of phenylbutyric acid; the author has subjected these to a further examination in order, if possible, to separate them into optically active compounds. In this he has been unsuccessful; but a number of interesting derivatives have been obtained which are described in the present paper.

*Barium phenyltrihydroxybutyrate*,  $(C_{10}H_{11}O_5)_2Ba$ , is obtained by the action of boiling baryta water on the lactone, and forms slender needles. The *strychnine salt*,  $C_{21}H_{22}N_2O_2 \cdot C_{10}H_{12}O_5 + H_2O$ , crystallises in microscopic needles or plates, loses its water of crystallisation at  $95^\circ$ , and becomes yellow at  $105^\circ$ . *Nitrophenyltrihydroxybutyrolactone* is obtained by the action of nitric acid of sp. gr. 1.5 on the lactone of the trihydroxy-acid, and crystallises in slender, colourless needles melting at  $185^\circ$  with slight evolution of gas; on boiling with alkalis

it first dissolves, after which a crystalline, yellow precipitate suddenly separates. *Phenylamidodihydroxybutyric anhydride*, prepared by boiling phenylbromhydroxybutyrolactone with ammonia for a short time, forms well-developed, colourless prisms which have a neutral reaction, become brown at 200°, and melt at 215°. It is not altered by boiling with alkalis or heating with phenylhydrazine, and it is therefore uncertain whether it is a lactone or a lactam. *Phenylbromodihydroxybutyranilide*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CHBr}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NHPh}$ , obtained by heating the bromolactone with aniline at 100°, crystallises in slender needles melting at 167—168° (uncorr.), and the *phenylhydrazide*, obtained by the action of phenylhydrazine in the cold, forms microscopic, rhombus-shaped plates melting and decomposing at 168—169°. If the bromolactone is warmed with phenylhydrazine, it is converted into *phenylhydroxybenzylhydrozypyrazolidone*, which has probably the constitution  $\text{CO} < \begin{array}{c} \text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CHPhOH} \\ \text{NH} \text{---} \text{NPh} \end{array}$ , and crystallises in spherical aggregates of colourless needles melting at 208°.

When the bromolactone is reduced with sodium amalgam, it yields two products having the composition  $\text{C}_{10}\text{H}_{10}\text{O}_3$  and  $\text{C}_{10}\text{H}_{10}\text{O}_2$  respectively. The former is probably a *phenylhydroxybutyrolactone*, and may be a stereoisomeride of the compound described under the same name by Biedermann (Abstr., 1892, 471). It crystallises from ether in colourless needles, melts at 124—126°, and gives a white crystalline precipitate with phenylhydrazine in ethereal solution. The second compound, separated by means of its solubility in light petroleum, crystallises in large, colourless needles melting at 87—88°, and behaves towards phenylhydrazine in the same manner as the previous compound. Its constitution is unknown. H. G. C.

**The Law of Etherification of Aromatic Acids.** By V. MEYER and J. J. SUDBOROUGH (*Ber.*, 1894, 27, 3146—3153; compare Abstr., 1894, i, 463).—The nitrophthalic acids behave similarly to substituted benzoic acids as regards the formation of ethereal salts.

Dinitrophthalic acid [ $\text{NO}_2 : \text{COOH} : \text{COOH} : \text{NO}_2 = 1 : 2 : 3 : 4$ ] gives no ethereal salt, whilst the acid [ $\text{NO}_2 : \text{COOH} : \text{COOH} : \text{NO}_2 = 1 : 3 : 4 : 5$ ] yields monalkylic salts. 1 : 2 : 6-Dinitrobenzoic acid gives no ethereal salt.

Tetrachlorophthalic acid, however, yields small quantities of the normal methylic salt, but as the behaviour of 2 : 4 : 6-trichlorobenzoic acid is normal, the authors conclude that the normal methylic salt is analogous in structure to phthalyl chloride, and cannot, therefore, be regarded as a true ethereal salt. Both 2 : 4 : 5- and 3 : 4 : 5-trichlorobenzoic acids yield an ethylic salt. 2 : 4 : 6-Trichlorobenzoic acid was prepared from trichloraniline instead of tribromaniline. M. O. F.

**Introduction of Acid Radicles into Ethylic Benzoylacetate.** By A. BERNHARD (*Annalen*, 1894, 282, 153—191).—When ethylic cuprobenzoylacetate is treated with benzoic chloride, three substitution compounds are produced. Ethylic dibenzoylacetate, or ethylic  $\alpha$ -benzoyl- $\beta$ -hydroxycinnamate,  $\text{OH}\cdot\text{CPh}\cdot\text{CBz}\cdot\text{COOEt}$ , has been prepared.

viously described (Trans., 1891, 1000), and is converted by bromine into ethylic bromodibenzoylacetate. The copper compound crystallises from alcohol in needles melting at 221°.

*Ethylic  $\alpha$ -benzoyl- $\beta$ -benzoxy cinnamate*,  $\text{OBz}\cdot\text{CPh}\cdot\text{CBz}\cdot\text{COOEt}$ , constitutes about one-half of the neutral products formed by the above reaction. It crystallises from ether in thick prisms, melts at 98°, and is readily soluble in hot alcohol, &c. It gives no coloration with ferric chloride, and is only slowly decomposed by warming with aqueous soda. When treated with sodium ethoxide, it yields ethylic benzoate, together with ethylic  $\alpha$ -benzoyl- $\beta$ -hydroxycinnamate. A similar change is produced by phenylhydrazine, benzoylhydrazine being formed. Bromine also acts in a somewhat similar manner, benzoic bromide and *ethylic  $\alpha$ -bromodibenzoylacetate*,  $\text{CBrBz}_2\cdot\text{COOEt}$ , being produced. The latter crystallises in elongated tablets, and melts at 109—110°. The same bromo-compound is formed directly by the action of bromine on ethylic dibenzoylacetate and ethylic  $\alpha$ -benzoyl- $\beta$ -acetoxy cinnamate. The remainder of the neutral oil referred to above probably consists of *ethylic  $\beta$ -benzoxy isocinnamate*,  $\text{OBz}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COOEt}$ , although this has not yet been isolated from it in the pure state.

Benzoic chloride reacts in a precisely similar manner with ethylic sodiobenzoylacetate, the action being in both cases exactly analogous to that of benzoic chloride on ethylic acetoacetate (Nef, Abstr., 1894, i, 628).

When ethylic cuprobenzoylacetate is treated with two-thirds of the calculated amount of acetic chloride, the product consists of ethylic  $\beta$ -acetoxy isocinnamate, and a small amount of ethylic benzoyl-acetoacetate, together with some regenerated ethylic benzoylacetate. *Ethylic benzoylacetate* (ethylic  $\alpha$ -benzoyl- $\beta$ -hydroxycrotonate),  $\text{OH}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{COOEt}$ , has been previously described by Bonné (this Journal, 1887, ii, 437). *Ethylic  $\beta$ -acetoxy isocinnamate*,



is a neutral substance, and crystallises in long needles melting at 27—28°. It reacts with sodium ethoxide in alcoholic solution to form ethylic acetate and ethylic sodiobenzoylacetate, and behaves in a similar manner with phenylhydrazine, acetylphenylhydrazine being produced.

*Ethylic  $\alpha$ -benzoyl- $\beta$ -acetoxy crotonate*,  $\text{OAc}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{COOEt}$ , is obtained by the action of acetic chloride on the copper compound of ethylic benzoylacetate as a neutral, unstable, brown oil, which is readily decomposed by dilute soda, gives a red coloration with alcoholic ferric chloride when left for a few minutes in contact with it, and reacts with sodium ethoxide to form ethylic acetate and ethylic sodiobenzoylacetate.

Ethylic chloroformate reacts with the sodium and copper compounds of ethylic benzoylacetate to form ethylic benzoylmalonate and ethylic  $\beta$ -carbethoxy isocinnamate, a small amount of ethylic dibenzoylsuccinate (Perkin, jun., Trans., 1883, 263) being also formed in the second case.

*Ethylic benzoylmalonate*,  $\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{COOEt})_2$ , is a yellowish oil,

which boils at 192—193° under a pressure of 13 mm. It has strongly acid properties, dissolves in sodium carbonate, and gives a red coloration with alcoholic ferric chloride immediately. When distilled with steam, it decomposes quantitatively into ethylic benzoylacetate, carbonic anhydride, and alcohol. Sodium ethoxide, in alcoholic solution, produces the *sodium derivative*, which is a fine, white powder, and reacts with copper acetate yielding the *copper derivative*, which crystallises in dark green needles melting at 180°.

*Ethylic carbethoxyisocinnamate*,  $\text{COOEt} \cdot \text{O} \cdot \text{CPh} : \text{CH} \cdot \text{COOEt}$ , is a neutral, viscid, yellow oil, which boils at 200—202° under a pressure of 15 mm. It gives no coloration with ferric chloride until the mixture has stood for a considerable time. With sodium ethoxide, it forms ethylic carbonate and ethylic sodiobenzoylacetate, and reacts with phenylhydrazine in an analogous manner, ethylic benzoylacetate, ethylic carbazinate, and 1 : 3-diphenylpyrazolone (m. p. 135°) having been isolated from the product.

It is noteworthy that almost equal quantities of the neutral and acid products are formed by the action of ethylic chloroformate on ethylic sodiobenzoylacetate, whilst with the corresponding derivative of ethylic acetoacetate, the neutral compound is the chief product.

*The action of acid anhydrides on ethylic benzoylacetate* proceeds in a manner very similar to that of the acid chlorides, as will be seen from the following summary of the products obtained. (1) Acetic anhydride yields ethylic benzoylacetoacetate (20—30 per cent.), a mixture of ethylic  $\beta$ -acetoxyisocinnamate, and ethylic  $\alpha$ -benzoyl- $\beta$ -acetoxy-crotonate (20 per cent.), acetophenone (15 per cent.), acetic acid, ethylic acetate, and ethylic benzoylacetate (18—32 per cent.). (2) Benzoic anhydride yields ethylic dibenzoylacetate (50 per cent.), small amounts of tribenzoylmethane and ethylic dehydrobenzoylacetate, ethylic benzoate, benzoic acid, and possibly ethylic  $\beta$ -benzoxyisocinnamate.

Acetic anhydride also acts on ethylic oxalacetate to form *ethylic  $\beta$ -acetoxyfumarate*, which is a neutral oil, gives no coloration with ferric chloride, and reacts with phenylhydrazine to form acetylphenylhydrazine.

The author is of opinion that the difference in behaviour towards alkalis of the two forms of tribenzoylmethane and dibenzoylacetone may be due to physical causes, and is not necessarily to be ascribed to a difference in chemical constitution (compare Claisen, *Abstr.*, 1894, i, 192).

Two formulæ are possible for the derivatives of the  $\beta$ -ketonic acids which contain two acid radicles such as ethylic dibenzoylacetoacetate,  $\text{C}(\text{AcBz})_2 \cdot \text{COOEt}$  and  $\text{OBz} \cdot \text{CMe} : \text{CBz} \cdot \text{COOEt}$ . Both formulæ equally express the neutral character of the compound; if the former of the two formulæ were correct, the same substance should be obtained by the action of acetic chloride on ethylic dibenzoylacetate, and of benzoic chloride on ethylic benzoylacetoacetate, whereas, according to the second formula, two different compounds should be produced.

Experiment shows that the latter is what actually occurs, ethylic

$\alpha$ -benzoyl- $\beta$ -acetoxycinnamate and ethylic  $\alpha$ -benzoyl- $\beta$ -benzoxycrotonate respectively being formed. The same view is further confirmed by the fact that sodium ethoxide, phenylhydrazine, and bromine always replace that acid radicle which has been last introduced.

If this formula be accepted, there are still two stereoisomeric configurations possible, but at present it is impossible to decide between them with any approach to certainty. A. H.

**Vinyltriphenylsulphone (Triphenylsulphonethane).** By R. OTTO (*Ber.*, 1894, 27, 3055—3058).—When monochlorethylene dichloride is warmed with sodium benzenesulphinate in alcoholic solution, it yields, not a trisulphone, but the disulphone,  $C_2H_4(SO_2Ph)_2$ , sodium sulphate and benzenesulphonate being simultaneously formed. When warmed with sodium phenyl mercaptide, NaSPh, in alcoholic solution, however, it yields *vinyltrithiophenyl (trithiophenylethane)*,  $SPh \cdot CH_2 \cdot CH(SPh)_2$ . This is an oil having an odour resembling that of lemons; when oxidised with permanganate, it yields ethylenediphenylsulphone and a benzenesulphonate, but, if care is taken to avoid a rise of temperature, *vinyltriphenylsulphone (triphenylsulphonethane)*,  $SO_2Ph \cdot CH_2 \cdot CH(SO_2Ph)_2$ , is formed. This is insoluble in water; it is readily hydrolysed by aqueous soda, apparently with formation of glycollic aldehyde. C. F. B.

**Indigo.** By C. J. VAN LOOKEREN and P. J. VAN DER VEEN (*Landw. Versuchs-Stat.*, 1894, 43, 401—426).—The authors have prepared indican from the leaves of plants belonging to the species *Indigofera*, and their results are identical with those obtained by Schunck in his experiments with *Isatis tinctoria* (woad). The sugar, which the authors obtained as a syrup by hydrolysing their indican, was dextro-rotatory, reduced Fehling's solution, gave a brown coloration with alkalis, and was probably identical with ordinary glucose (dextrose). The so-called indigo-gluten is probably a mixture of nitrogenous decomposition products of indican, with a certain amount of the enzyme (rendered inactive) which determines the hydrolysis of indican. Schunck's oxindicanin gives a red precipitate when warmed with Millon's reagent. Experiments are next described which point to the existence of an enzyme as the hydrolyst of indican, thus the hydrolysis of indican proceeds under conditions which exclude the presence of micro-organisms. The quality of the indigo-blue is affected by continuing the lixiviation process too long, which is done in practice, and the cause of this may be the action of bacteria. If the so-called fermentation is protracted, the indigo-blue contains a larger proportion of calcium salts and more indigo-gluten. According to the authors, the usual practice is to employ water at a temperature of  $27.5^\circ$  for the fermentation; better results are obtained by digesting with water at an initial temperature of  $55^\circ$ , the digestion (fermentation) being continued for about seven hours at a temperature of about  $28^\circ$ . The authors find that in the manufacture of indigo-blue, equivalent quantities of lime, potash, or soda may be used instead of ammonia. A. R. L.

**Parahydrazidodiphenyl.** By H. MÜLLER (*Ber.*, 1894, 27, 3105—3108).—*Parahydrazidodiphenyl*,  $C_{12}H_9 \cdot NH \cdot NH_2$ , is prepared by diazotising paramidodiphenyl and reducing the diazo-compound with tin and hydrochloric acid, the *hydrochloride* thus formed being decomposed by alkali and the free base extracted with ether; after crystallisation from hot alcohol, it forms lustrous, colourless plates, melts at  $135\text{--}136^\circ$  (uncorr.), and quickly oxidises in the air, especially when moist. The *hydrochloride*, *sulphate*, and *nitrate* all crystallise in colourless plates, and are sparingly soluble in cold water. The *acetyl* derivative,  $C_{12}H_9 \cdot N_2H_2Ac$ , crystallises in colourless plates melting at  $203^\circ$ , and the *thiocarbamide*,  $C_{12}H_9 \cdot N_2H_2 \cdot CS \cdot NHPh$ , in colourless needles melting at  $182^\circ$ ; the latter dissolves in concentrated sulphuric acid with a deep blue colour.

Parahydrazidodiphenyl readily combines with aldehydes and ketones, including the sugars, but the compounds obtained from the latter do not crystallise well, and are, therefore, of no use for the recognition or isolation of the sugars. *Acetonehydrazonediphenyl*,  $C_{12}H_9 \cdot NH \cdot N : CMe_2$ , is crystalline, melts at  $86\text{--}87^\circ$ , and yields an indole when heated at  $180^\circ$  with zinc chloride. *Acetophenonehydrazonediphenyl*,  $C_{12}H_9 \cdot NH \cdot N : CMePh$ , forms colourless plates melting at  $148^\circ$ , and *benzylidenehydrazidodiphenyl*,  $C_{12}H_9 \cdot NH \cdot N : CHPh$ , crystallises in yellowish needles melting at  $153^\circ$ . *Arabinosehydrazonediphenyl*,  $C_{12}H_9 \cdot NH \cdot N : C_5H_{10}O_4$ , is obtained with difficulty in nodular aggregates of slender crystals, and melts, when quickly heated, at  $138\text{--}140^\circ$ , with decomposition. The *xylose* derivative has similar properties. *Glucosehydrazonediphenyl*,  $C_{12}H_9 \cdot NH \cdot N : C_6H_{12}O_5$ , forms very slender crystals, melts at  $143\text{--}144^\circ$  with evolution of gas, and, on heating with an excess of the hydrazine, yields the *osazone*. *Galactosehydrazonediphenyl* crystallises in stellate groups of colourless needles melting and decomposing at  $157\text{--}158^\circ$ . H. G. C.

**Stereoisomeric Paraphenylhexahydrobenzoic acids.** By B. RASSOW (*Annalen*, 1894, 282, 139—153).—*Paraphenylhexahydrobenzoic acid*,  $C_6H_{10} \cdot Ph \cdot COOH$ , may be prepared by reducing paradiphenylcarboxylic acid with sodium and boiling amyl alcohol, or by treating the same acid with sodium amalgam in alkaline solution, whereby it is converted into a mixture of tetrahydro-acids, acting on these with hydrobromic acid, and finally reducing the hydrobromides thus obtained by means of sodium amalgam. The crude hexahydro-acid melts at  $190\text{--}195^\circ$ ; but on crystallisation yields an acid, which melts at  $202^\circ$ , together with a portion of lower melting point, from which an acid, melting at  $113^\circ$ , may be isolated in small quantity by extracting with boiling water, filtering, and adding potassium permanganate to the solution in sodium carbonate until a permanent coloration is produced.

Paraphenylhexahydrobenzoic acid (m. p.  $202^\circ$ ) crystallises from dilute acetic acid or ether in lustrous plates. The *silver* salt is insoluble in water, the *sodium* and *ammonium* salts sparingly soluble, and the *potassium* salt readily soluble. A solution of the ammonium salt gives white, insoluble precipitates with barium chloride, calcium chloride, zinc sulphate, and mercuric chloride, whilst the *magnesium*

salt dissolves in hot water. The *methylic salt*, prepared by treating the chloride with methylic alcohol, forms tabular crystals, and melts at 28—30°. On oxidation with potassium permanganate, the hexahydro-acid is converted into a *hydroxy-acid*, which probably has the formula  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}\cdot\text{COOH}$ . It forms a honey-like mass, with an ill-defined melting point of about 145°. This hydroxy-acid loses a molecule of water when boiled with water, a *tetrahydrophenylbenzoic acid* being formed, which melts at 158°, and, since it is not altered by boiling with aqueous soda, is probably a  $\Delta^{1,2}$ -acid. It at once decolorises alkaline potassium permanganate, and combines with bromine. The *silver salt* of the hydroxy-acid also loses a molecule of water when boiled with water, yielding the *salt* of the tetrahydro-acid. More thorough oxidation converts the hexahydro-acid into benzoic acid.

*Isoparaphenylhexahydrobenzoic acid* (m. p. 113°) is best obtained by heating the acid of higher melting point with fuming hydrochloric acid at 170—180°. It forms lustrous needles, and dissolves in about 1000 parts of boiling water. The *silver salt* blackens when heated in contact with the solution from which it has been obtained, and is somewhat soluble in hot water. The *sodium*, *potassium*, and *ammonium* salts are all readily soluble in water, and the *calcium* salt moderately so. When the iso-acid is heated with fuming hydrochloric acid, it is partially reconverted into the acid of higher melting point, the same state of equilibrium being reached from either acid, that of higher melting point constituting about 90 per cent. of the mixture. The iso-acid is also converted into benzoic acid by oxidation.

The paper is prefaced by a note by Baeyer, in which he points out that it has been found impossible to obtain stereoisomeric forms of tetrahydro- $\alpha$ - and  $\beta$ -naphthoic acids, and that this result, although, as it is negative, it cannot be considered decisive, is in favour of the view that the valencies of the 6 hydrogen atoms of the benzene ring are perfectly symmetrically arranged.

The results described in the foregoing paper show that in the closely related hexahydrophenylbenzoic acid the differences between the properties of the two stereoisomerides are quite well marked.

A. H.

**Tetramethyldiamidodiphenylmethane.** By J. PINNOW (*Ber.*, 1894, **27**, 3161—3167).—The action of nitrous acid on tetramethyldiamidodiphenylmethane converts it into a mononitro-derivative, which melts at 87—88°. The further action of nitrous acid gives rise to a *dinitro*-derivative, which crystallises in slender, red needles, and melts at 123—124°. An *isomeride* is produced when a mixture of nitric and sulphuric acids is added to the solution of tetramethyldiamidodiphenylmethane in concentrated sulphuric acid; it crystallises from glacial acetic acid in red prisms, which melt at 191·5° (uncorr.). This compound yields *tetramethyltetramidodiphenylmethane* when reduced with tin and hydrochloric acid; the base crystallises in colourless needles, which melt at 142° (uncorr.). The action of nitric acid on tetramethyldiamidodiphenylmethane in glacial acetic acid solution leads to the formation of nitrosamines and nitramido-derivatives;



*dimethyldinitrosamidodiphenylmethane* is produced on adding sodium nitrite to the solution of the base in hydrochloric acid (sp. gr. 1.19). It crystallises in slender, pale yellow needles, which melt at 101.5°. A condensation product of tetramethyldiamidodiphenylmethane with formaldehyde appears to be formed when a mixture of dimethylaniline (10 grams), formaldehyde solution (10 grams), and glacial acetic acid (15 grams) is boiled for eight hours; it has the composition  $(C_{18}H_{22}N_2)x$ .

With diazobenzenesulphonic acid, tetramethyldiamidodiphenylmethane yields a colouring matter, which, on reduction with tin and hydrochloric acid, is resolved into paramidodimethylaniline and paramidobenzenesulphonic acid.

M. O. F.

### Constitution of the Alkali Compounds of Phenolphthaleïn.

By E. HJELT (*Chem. Zeit.*, 1894, 18, 3).—According to Armstrong (*Proc.*, 1893, 52), the coloured salts of the phthaleïns assume a quinonoid structure; this view presupposes, for example, in the case of phenolphthaleïn, that the phthalide ring (lactone ring) is readily disrupted by alkalis. The author's experiments indicate, however, that the hydrolysis of the phthalide ring,  $C_6H_4 < \begin{smallmatrix} CR_2 \\ CO \end{smallmatrix} > O$ , proceeds much more slowly in the case of phthalide and of meconine than in the case of the aliphatic lactones (Henry, *Abstr.*, 1892, 1303). According to the formula  $Ac = \frac{x}{(A - x)t}$  ( $t$  in minutes), the following values were found; for phthalide,  $Ac = 0.0674$  ( $A = 10.1$ ); and for meconine,  $Ac = 0.0298$  ( $A = 11.2$ ). The hydroxy-acid corresponding with phenolphthaleïn is unknown, and is probably incapable of existence.

A. R. L.

**Synthesis and Constitution of Vulpic acid.** By J. VOLHARD (*Annalen*, 1894, 282, 1—21).—According to Spiegel (*Abstr.*, 1881, 97, 173, 1036; 1882, 1076), vulpic acid is the monomethylic salt of the bibasic pulvic acid, which is converted by alkalis into dibenzylglycollic acid,  $OH \cdot C(CH_2Ph)_2 \cdot COOH$ , a diketonic acid, symmetrical diphenylketipic acid,  $COOH \cdot CHPh \cdot CO \cdot CO \cdot CHPh \cdot COOH$ , being formed as an intermediate product.

In order to prepare vulpic acid synthetically, the author starts from benzylic cyanide, which is converted by ethylic oxalate and sodium ethoxide in alcoholic solution into the *dinitrile* of *diphenylketipic acid*,  $CN \cdot CHPh \cdot CO \cdot CO \cdot CHPh \cdot CN$ . This substance crystallises from amyl alcohol in olive-green, lustrous scales, and melts and decomposes at 270°. When hydrolysed with 60 per cent. sulphuric acid, the nitrile is converted into pulvic acid dilactone (70 per cent.), and pulvic acid (14—18 per cent.), a small amount of other products of unknown nature being also formed. When the dilactone is treated with a solution of potash in methylic alcohol and the solution acidified, vulpic acid is obtained, identical with that prepared from *Evernia vulpina*.

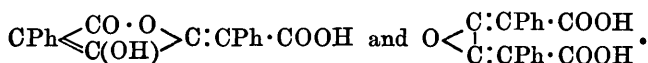
*Piperidinæ vulpate* forms long, thin, yellow needles melting at 139—142°.

The pulvic acid prepared from the dilactone is also identical in every respect with that obtained by Spiegel. It crystallises with  $1\text{C}_2\text{H}_5\text{O}$  in yellowish-red, rhombic prisms, which have the axial ratio  $0.5835 : 1 : 0.4337$ .

*Monobromopulvic acid*,  $\text{C}_{18}\text{H}_{11}\text{BrO}_5$ , crystallises in radial groups of yellow tablets, melts at  $208\text{--}209^\circ$ , and forms a crystalline *barium salt*.

*Dibenzylolalylcarboxylic acid lactone*,  $\text{CHPh}\cdot\text{C} \begin{smallmatrix} \text{CO}\cdot\text{CHPh} \\ \text{O}-\text{CO} \end{smallmatrix}$ , is contained among the products of hydrolysis of the dinitrile. It forms small needles, and melts at  $231\text{--}233^\circ$ .

It follows from this synthesis that pulvic acid is the anhydride of diphenylketipic acid, but it is at present impossible to decide between the formulæ



A. H.

**Pulvamic acids and Ethereal Salts of Pulvic acid.** By R. SCHENCK (*Annalen*, 1894, **282**, 21—44; compare the foregoing abstract).—Pulvamic acid has previously been described by Spiegel (*Abstr.*, 1881, 1076). The *ammonium salt* melts at  $218^\circ$ , and the *potassium salt* crystallises in slender needles with  $5\text{H}_2\text{O}$ , whilst the *zinc* and *silver salts* are insoluble and amorphous. It appears to be impossible to displace a second hydroxyl-group in the molecule by the amido-group.

*Pulvomethylamic acid*,  $\text{C}_{19}\text{H}_{15}\text{O}_4\text{N}$ , is obtained by the action of methylamine on the dilactone. It crystallises in quadratic plates, and melts at  $237^\circ$ . The *methylamine salt* melts at  $214^\circ$ . The *barium salt* is sparingly soluble in water. *Pulvanilic acid*,  $\text{C}_{22}\text{H}_{17}\text{O}_4\text{N}$ , forms compact crystals, and melts at  $187\text{--}188^\circ$ . The *ammonium salt* melts at  $153^\circ$ ; the *potassium salt* forms yellow crystals with  $2\text{H}_2\text{O}$ . *Pulv-anaphthylamic acid* crystallises in iridescent, reddish-yellow plates, and melts at  $211\text{--}212^\circ$ . The *ammonium salt* melts at  $208^\circ$ , and the *barium salt* crystallises from alcohol in slender needles. *Pulvo-β-naphthylamic acid* forms druses of large, reddish-yellow crystals, and melts at  $192^\circ$ . The *ammonium salt* melts indefinitely at about  $182^\circ$ . The *barium salt* forms a crystalline powder.

Methylaniline and diphenylamine do not yield amic acids. *Pulv-dimethylamic acid* crystallises in small prisms, and melts at  $211^\circ$ , its *dimethylamine salt* melting at  $210^\circ$ . The acid is quite analogous to pulvamic and pulvomethylamic acids. *Pulvopiperidinic acid* is very unstable, and melts at from  $150^\circ$  to  $160^\circ$ . Its *piperidine salt* melts at  $199\text{--}220^\circ$ . The metallic salts are decomposed by boiling with water, piperidine being formed. *Pulvhydroxamic acid* is obtained by heating the dilactone with hydroxylamine hydrochloride, sodium acetate, and acetic anhydride. It crystallises in quadratic plates, and melts at  $194^\circ$ , with evolution of carbonic anhydride; the acid is bibasic to baryta water. Its *monaniline salt* forms plates melting at  $163\text{--}164^\circ$ . *Pulvophenylhydrazinic acid* melts at  $201\text{--}202^\circ$ , and forms

a *phenylhydrazine salt*, which is more readily soluble in alcohol, and melts at the same temperature. The *ammonium salt* forms pale yellow, slender needles, and melts at 187—188°.

The mon-etheral salts of pulvic acid may be obtained by the action of potash and an alcohol on the dilactone, or by that of an alkyl iodide on the hydrogen silver salt. The normal etheral salts form compounds with 1 mol. water and 1 mol. piperidine.

The following have been prepared.

	M. p.	M. p. of piperidine compound.
Methylic vulpate.....	141°	147—148°
Ethylic vulpate .....	138—139	152—153
Methylic ethylpulpate....	150—151	151
Propylic vulpate .....	95—96	149
Methylic propylpulpate ..	121—122	126
Propylpulvic acid.....	134	—

Ammonia reacts with the normal etheral salts to form an amide and phenylacetic acid. The amide,  $C_{10}H_8O_2N_2$ , crystallises in bronze-coloured plates, and melts at 247·5°. When boiled with dilute hydrochloric acid, it yields cyanophenylpyruvic acid (compare the following abstract). A. H.

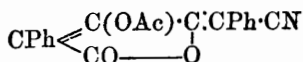
**Derivatives of Diphenylketipodinitrile.** By J. VOLHARD and F. HENKE (*Annalen*, 1894, **282**, 45—84; compare the two preceding abstracts).—The hydrolysis of the dinitrile occurs in several stages. *Diphenylketipamidonitrile*,  $CN \cdot CPh : C(OH) \cdot C(OH) : CPh \cdot CO \cdot NH_2$ , is obtained by treating the dinitrile in the cold with concentrated sulphuric acid. It forms pale yellow needles containing 1 mol.  $C_2H_6O$ , and melts and decomposes at 199—200°; it gives a brownish-red coloration with alcoholic ferric chloride. When boiled with aqueous sodium carbonate, the nitrile is decomposed into benzylic cyanide and hydroxyphenylmaleinimide,  $C_{10}H_7NO_3$ , which is described later on.

*Diphenylketipamidonitrilesulphonic acid*,  $C_{18}H_{13}O_3N_2 \cdot SO_3H$ , is obtained by warming a solution of the dinitrile in sulphuric acid on the water bath. It forms microscopic, flat needles, and does not melt below 300°. The *sodium* and *barium salts* are both crystalline.

No diamido-compound was observed among the products of hydrolysis of the dinitrile, but a small amount of pulvamic acid (compare the preceding abstract) is formed. This substance can also be readily obtained by boiling the amidonitrile with hydrochloric acid. The *methylic salt* forms almost colourless, compact crystals melting at 216—217°. When this salt is hydrolysed, pulvic acid, and not an isomeride of vulpic acid, is formed.

The dinitrile readily dissolves in alcoholic potash, forming a *potassium salt*,  $C_{18}H_{12}O_2N_2K_2 + 2C_2H_6O$ , which crystallises in colourless plates. The *sodium salt* may be prepared in a similar manner. The dinitrile also appears to form an unstable compound with 1 mol. HCl. The *monacetate*,  $CN \cdot CPh : C(OAc) \cdot C(OH) : CPh \cdot CN$ , is obtained by the action of a mixture of acetic acid and acetic anhydride;

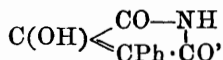
it crystallises in lustrous needles, and melts at 208—209.5°. It is insoluble in water, but dissolves in aqueous alkalis, the *sodium salt* crystallising with 3H<sub>2</sub>O in scarlet needles. The *methylic salt*, prepared from the amorphous red *silver salt*, crystallises in lustrous, yellow needles, and melts at 229—231°. When heated with aqueous ammonia at 100°, the acetate yields benzylic cyanide and phenylacetamide, together with oxalic and oxamic acids. Acetic and benzoic chlorides act on the sodium and silver salts, but only reproduce the monacetate. The *diacetate* is formed when the dinitrile is treated with pure acetic anhydride, and forms greyish-green needles melting at 177—179°. It is insoluble in water and alkalis, and combines with 1 mol. of alcohol to form a *compound*, which can be recrystallised from toluene, and melts at 191—191.5°. Methylic alcohol forms a similar *compound*, which crystallises in colourless granules, and melts and decomposes at 196°. The *compound* with amylic alcohol crystallises in very slender needles. Acetic chloride reacts with the dinitrile to yield the monacetate together with the *monacetate* of the lactone of the semi-hydrolysed dinitrile,



This crystallises in canary-yellow needles, and melts at 141—142°. The corresponding *benzoate* crystallises in slender, yellowish needles, melting at 168—168.5°. The *monobenzoate* of the dinitrile is also formed in dark, orange-red granules, melting at 220—224°, which dissolve in alkalis. Phosphorus oxychloride converts the dinitrile into a *chloro-derivative*,  $\text{CPh} \begin{array}{l} \swarrow \text{CCl} \cdot \text{C} \cdot \text{CPh} \cdot \text{CN} \\ \searrow \text{CO} \quad \text{O} \end{array}$ , corresponding

in composition with the lactone compounds described above. It crystallises in long, greyish-green needles, and melts at 161—162°. It is insoluble in water and aqueous alkalis, but dissolves in alcoholic potash, and yields a crystalline *barium salt*. When heated with sodium acetate and alcohol, it loses chlorine, forming a *hydroxy-compound* of the formula C<sub>18</sub>H<sub>11</sub>O<sub>3</sub>N, which crystallises in matted, reddish-yellow needles, and melts at 193—194°. When heated with acetic anhydride, this is converted into the acetate of the semi-lactone already described.

Dilute alcoholic ammonia at 100° converts the dinitrile into an *isocyanophenylpyruvamide*,  $\text{C(OH)} \begin{array}{l} \swarrow \text{C(NH)} \cdot \text{NH} \\ \searrow \text{CPh} \quad \text{CO} \end{array}$ , which crystallises in red needles, and does not melt below 280°. It dissolves in alkalis, and forms crystalline *sodium* and *barium* salts. Amylic nitrite converts it into a *nitro-derivative*, C<sub>10</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>·NO<sub>2</sub>, which melts and decomposes at 246°. When heated with dilute hydrochloric acid, it is very readily converted into *hydroxyphenylmaleinimide*,



which is best prepared by heating the amidonitrile or its sulphonic

acid with aqueous sodium carbonate. It crystallises in lustrous, yellow scales, melts at  $216-218^{\circ}$ , gives a green coloration with ferric chloride, and forms salts with one equivalent of metal. The *ethylic salt* crystallises in long, lustrous needles, resembling the salts of uranium in appearance, and melting at  $128-130^{\circ}$ . This substance is isomeric with the ethylic phenylcyanopyruvate described by Erlenmeyer, jun. (*Annalen*, 1892, 271, 172). The latter compound, on hydrolysis, yields a substance which was described by Erlenmeyer as phenylcyanopyruvic acid, but which is identical with hydroxyphenylmaleinimide. This substance cannot have the constitution ascribed to it by Erlenmeyer, as, when its silver salt is treated with ethylic iodide, it yields the yellow ethereal salt described above, and not the original colourless ethylic phenylcyanopyruvate,  $\text{CN}\cdot\text{CPh}\cdot\text{CO}\cdot\text{COOEt}$ , by the hydrolysis of which it was obtained. It is, moreover, converted by ammonia into the phenylamidomaleinimide described below. Acetic anhydride converts hydroxyphenylmaleinimide into the *acetate*,  $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3\text{Ac}$ , which crystallises in long, white needles melting at  $134-135^{\circ}$ . *Ethoxyphenylmalein-benzoylimide*,  $\text{C}_{19}\text{H}_{15}\text{O}_4\text{N}$ , prepared by treating the yellow ethylic salt with benzoic chloride, crystallises in yellowish needles with a greenish fluorescence, and melts at  $105-106^{\circ}$ . The isomeric *benzoyl-derivative* obtained from Erlenmeyer's ethylic phenylcyanopyruvate crystallises in colourless prisms, and melts at  $102-103^{\circ}$ .

*Phenylamidomaleinimide*,  $\text{NH}_2\cdot\text{C} \begin{smallmatrix} \text{CO}-\text{NH} \\ \diagup \quad \diagdown \\ \text{CPh}\cdot\text{CO} \end{smallmatrix}$ , is obtained by the action of alcoholic ammonia on ethoxyphenylmaleinimide, and has also been obtained from the chloro-semilactone described above, and from the neutral ethereal salts of pulvic acid, a proof that it contains no cyanogen group. It crystallises in thin, golden-yellow, lustrous plates, and melts at  $248-249^{\circ}$ . The corresponding *piperidide*,  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$ , is formed when ethoxyphenylmaleinimide is heated with piperidine, and crystallises in orange-coloured needles melting at  $155-156.5^{\circ}$ .

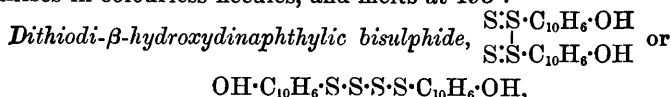
*Ethoxyphenylmaleic anhydride*,  $\text{C(OEt)} \begin{smallmatrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{CPh}\cdot\text{CO} \end{smallmatrix}$ , is formed when the imide is warmed with aqueous sodium carbonate. It crystallises in transparent, prismatic needles, and melts at  $97-98^{\circ}$ . The free acid corresponding with the anhydride cannot be obtained, but its salts are formed by dissolving the anhydride in boiling alkalis or alcoholic ammonia. The *ammonium salt*,  $\text{C}_{12}\text{H}_{10}\text{O}_5(\text{NH}_4)_2$ , melts at  $144-146^{\circ}$ , and the *sodium* and *barium* salts are both crystalline. Fuming hydriodic acid at  $165^{\circ}$  converts the anhydride into phenylsuccinic acid, which is a crystalline powder melting at  $160-161^{\circ}$  (stated by Spiegel as  $167^{\circ}$ ).

The formation of phenylamidomaleinimide from the ethereal salts of pulvic acid can best be explained by adopting Spiegel's view, that this acid is a hydroxy-lactone.

A. H.

**Thio-derivatives of  $\beta$ -Naphthol.** By R. HENRIQUES (*Ber.*, 1894, 27, 2993—3005).—By the action of sulphur chloride on  $\beta$ -naphthol in

chloroform solution, *di-β-hydroxydinaphthyl sulphide*,  $S(C_{10}H_6 \cdot OH)_2$ , is formed; it is sparingly soluble in chloroform and in carbon bisulphide, and separates in long, silky needles, or in colourless, transparent, highly lustrous, round crystals, and melts at  $211^\circ$ . With concentrated sulphuric acid, a bluish-green coloration is produced; with diazo-derivatives, sulphur is eliminated, and the ordinary azo-naphthol dyes are produced; the sulphur is not, however, removed by treatment with silver salts. The molecular weight was determined by the boiling point method. The compound is identical with that (m. p.  $214^\circ$ ) prepared by Dahl and Co. by heating  $\beta$ -naphthol, sulphur, and lead oxide at  $180$ – $200^\circ$ , and with the compound (m. p.  $210^\circ$ ) obtained by Lange (Abstr., 1888, 375) by heating naphthol with sulphur in alkaline solution, and to which he erroneously gives the formula  $S_2(C_{10}H_6 \cdot OH)_2$ . The *lead salt*,  $C_{20}H_{12}SO_2Pb$ , is yellow and amorphous; the *acetyl derivative*,  $S(C_{10}H_6 \cdot OAc)_2$ , crystallises in colourless needles, and melts at  $193^\circ$ .



is formed, together with the sulphide, from which it is separated by means of its greater solubility in carbon bisulphide, and is deposited in large, sulphur-coloured crystals, melting at  $141^\circ$ ; the yield is 15 per cent. of the naphthol employed. The compound is also formed by heating dihydroxydinaphthyl bisulphide (see below) with sulphur in alkaline solution; it is decomposed by silver salts, silver sulphide being precipitated, and dissolves in alkalis with an intense, yellow colour. The *lead salt*,  $C_{20}H_{12}S_4O_2Pb$ , is orange coloured; the *acetyl derivative*,  $C_{20}H_{12}S_4O_2Ac_2$ , crystallises in pale yellow needles, melting at  $164^\circ$ .

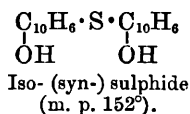
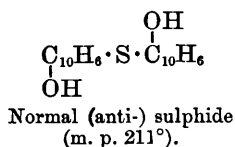
*Di-β-hydroxydinaphthyl bisulphide*,  $S_2(C_{10}H_6 \cdot OH)_2$ , is separated by means of its lead salt from the chloroform mother liquors obtained in the preparation of the preceding dithio-compound and sulphide; it readily dissolves in all organic solvents, in alkali carbonates, and in borax solutions, and crystallises in yellow needles, melting at  $166^\circ$ ; it is decomposed by silver salts. The *lead salt*,  $C_{20}H_{12}S_2O_2Pb$ , is orange coloured; the *acetyl derivative* resembles that of the preceding compound, and melts at  $194^\circ$ .

Dithiodihydroxydinaphthyl bisulphide and dihydroxydinaphthyl bisulphide give with potassium ferricyanide pale yellow, sparingly soluble ferricyanides; dihydroxydinaphthyl sulphide, in the same circumstances, is oxidised to *dehydrodi-β-hydroxydinaphthyl sulphide*,  $C_{20}H_{12}SO_2$ , which is deposited in large, red crystals, melting at  $155^\circ$ . The compound contains no hydroxyl, it dissolves in concentrated sulphuric acid with a dark blue colour, and readily reacts with hydroxylamine, although the products could not be isolated. The *phenylhydrazide*,  $S(C_{10}H_6 \cdot N_2HPh)_2$ , crystallises in brick-red needles, melting at  $184^\circ$ .

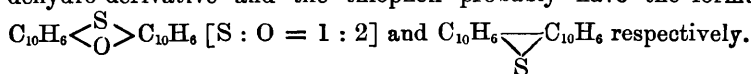
*Isodihydroxydinaphthyl sulphide* is prepared by the reduction of the preceding compound with zinc dust and glacial acetic acid; it crystallises in long, pale yellow needles, melts at  $152^\circ$ , is readily

soluble, and is easily converted into dihydroxydinaphthylic sulphide by heating with alkalis. With potassium ferricyanide, the dehydro-derivative is regenerated; by the action of diazo-compounds, azo-naphthols are formed and sulphur eliminated. The *silver salt* is colourless; the *lead salt*,  $C_{20}H_{12}SO_2Pb$ , resembles that of the isomeric compound; the *acetyl derivative* is crystalline, and melts at  $147-148^\circ$ .

*Dinaphthylenethiophen*,  $C_{20}H_{12}S$ , is prepared by the action of concentrated sulphuric acid on isodihydroxydinaphthylic sulphide at  $100^\circ$ , the sulphate dissolving with a blue-green colour, and evolution of sulphurous anhydride; the compound crystallises from glacial acetic acid in yellow needles, melts at  $147^\circ$ , is neutral, and boils without decomposing; the coloration produced with sulphuric acid is similar to that of the original sulphide. The yield is 60 per cent. of the sulphide employed. Dihydroxydinaphthylic sulphide gives no thiophen derivative. The author discusses in detail the constitution of dehydrodioxydinaphthylic sulphide and of isodihydroxydinaphthylic sulphide; the former, although generally resembling the quinones, differs from them in its behaviour towards phenylhydrazine and reducing agents; he considers that the two dihydroxydinaphthylic sulphides are stereoisomeric,



this is in complete accord with their behaviour, and, if correct, is the first example of simple stereoisomeric sulphur compounds. The dehydro-derivative and the thiophen probably have the formulæ



J. B. T.

**Preparation of 1 : 2-Naphthaquinone.** By K. LAGODZINSKI and D. HARDINE (*Ber.*, 1894, **27**, 3075—3076).—An improvement of the method of Stenhouse and Groves (this Journal, 1877, ii, 52). Fifty grams of 2-naphthol is dissolved in a solution of 14 grams of sodium hydroxide in 500 c.c. of water. The whole is then placed in a 3-litre vessel, diluted with 1 litre of water, and stirred with 25 grams of sodium nitrite; a large lump of ice (about 500 grams) is then added, and the stirring continued while 700 c.c. of 10 per cent. sulphuric acid is gradually added. After 2—3 hours, the precipitate is collected on a calico filter and washed with water until the washings have only a feebly acid reaction. It is then placed in a  $1\frac{1}{2}$ -litre flask, 300 c.c. of 10 per cent. sodium hydroxide added, and the whole diluted with water to 1,200 c.c., and warmed for a time on the water bath. Hydrogen sulphide is passed through the warm solution until white crystals of amidonaphthol begin to separate. These are collected on a porcelain funnel, washed with water, treated with 700 c.c.

of 5 per cent. sulphuric acid previously warmed to 70—80°, and filtered through a folded filter; the residual sulphur is washed with another 700 c.c. of the acid, and the united filtrates are cooled with a large lump of ice and oxidised with potassium dichromate. The 1:2-naphthoquinone, which then separates out in orange-yellow needles, is carefully washed until free from sulphuric acid. The yield is 47.5 grams, 86.6 per cent. of the theoretical. C. F. B.

**Derivatives of  $\alpha$ -Naphthylamine.** By C. BÖTTINGER (*Chem. Zeit.*, 1894, **18**, 483—484).—*Dichloracet- $\alpha$ -naphthalide* is prepared by moderately warming a mixture of dichloroacetic acid and  $\alpha$ -naphthylamine; it separates from ether in colourless crystals, and melts at 164°. *Glyceric- $\alpha$ -naphthalide* is obtained by warming  $\alpha$ -naphthylamine with an alcoholic solution of glyceric acid; it is crystalline, and melts at 137°; a secondary product (m. p. 214°) was also isolated in small amount. Pyruvic acid reacts with  $\alpha$ -naphthylamine in alcoholic solution, forming *pyruvic- $\alpha$ -naphthalide*, which melts at 148—149°.  *$\alpha$ -Naphthylamine hydrogen tartrate* melts and decomposes at 180°; *tartaric- $\alpha$ -naphthalide* crystallises in long, white needles, and melts at 210°, and  *$\alpha$ -naphthylamine citrate* crystallises in four-sided tablets, and melts at 146°. The citrate and tartrate of  $\alpha$ -naphthylamine have a burning taste. A. R. L.

**$\alpha$ -Dinaphthalidocitric acid.** By C. BÖTTINGER (*Chem. Zeit.*, 1894, **18**, 672).—Of the two theoretically possible modifications of  $\alpha$ -dinaphthalidocitric acid, one is obtained, together with other products, by heating a pulverised mixture of citric acid and  $\alpha$ -naphthylamine at 140°; it crystallises from boiling alcohol in white needles, and melts at 187—188°. If dissolved in nitric acid of sp. gr. 1.48, a yellow nitro-compound is formed, which yields intensely reddish-yellow alkali salts. When the acid is treated with acetic anhydride, a yellow compound is obtained, which is insoluble in soda and is probably an anhydro-compound. The silver salt of  $\alpha$ -dinaphthalidocitric acid is a white precipitate, insoluble in water, and very stable. A. R. L.

**1:2-Amidonaphtholsulphonic acids.** By M. BÖNIGER (*Ber.*, 1894, **27**, 3050—3054).—1:2:2'-Nitrosodihydroxynaphthalene, when heated with sodium hydrogen sulphite and hydrochloric acid, yields, by a reaction already described (*Abstr.*, 1894, i, 199), 1:2:2'-amido-dihydroxynaphthalene-4-sulphonic acid; this can be oxidised with nitrous acid to 2'-hydroxy-1:2-naphthaquinone-4-sulphonic acid, and this, with aniline, yields 2:2'-dihydroxy-4-anilidonaphthaquinone. 1:2:3-Nitrosohydroxynaphthalenesulphonic acid and 1:2:2'-nitrosohydroxynaphthalenesulphonic acid undergo an analogous series of reactions. C. F. B.

**Nomenclature of Cyclic Derivatives of Naphthalene.** By C. GRAEBE (*Ber.*, 1894, **27**, 3066—3068).—It is proposed that when, in compounds of the type of carbazole or anthracene, one phenylene group is replaced by naphthylene, the term "Naphtho-" (or



“Naphth-”) should be prefixed to the name of the parent substance; and that when both the phenylene groups are replaced by two naphthylene groups, the term “Dinaphtho” should be prefixed. Thus the compound  $C_{10}H_6 < \begin{smallmatrix} CO \\ O \end{smallmatrix} > C_6H_4$  would be termed *naphthoxanthone*, the compound  $C_{10}H_6 < \begin{smallmatrix} CO \\ O \end{smallmatrix} > C_{10}H_6$ , *dinaphthoxanthone*.

C. F. B.

**1 : 2-Dihydroxynaphtho-3 : 4-Acridone.** By K. LAGODZINSKI and D. HARDINE (*Ber.*, 1894, **27**, 3068—3075).—When 1 : 2-naphthaquinone is dissolved in acetic acid and the solution warmed with anthranilic acid, 2-hydroxynaphthaquinone-4-anilido-orthocarboxylic acid,  $C_{10}H_5O(OH):N \cdot C_6H_4 \cdot COOH$  [ $O : OH : N = 1 : 2 : 4$ ], is formed. This crystallises in dark red plates with a metallic lustre, and melts at  $270-271^\circ$ ; it yields no anhydride (acridone), but is hydrolysed by dilute mineral acids to 2-hydroxynaphthaquinone and anthranilic acid.

If a solution of anthranilic acid in water and alcohol is warmed with aqueous potassium 1 : 2-naphthaquinone-4-sulphonate, 1 : 2-naphthaquinone-4-anthranilic acid,  $C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot COOH$  [ $O_2 : NH = 1 : 2 : 4$ ], isomeric with the preceding compound, is formed. This crystallises in dark red needles, and melts at  $252^\circ$ ; its *methylic salt* forms brilliant, dark red crystals, which melt at  $188^\circ$ . When heated with strong sulphuric acid at  $200^\circ$ , it yields 1 : 2-naphthaquinone-3 : 4-acridone,  $C_{10}H_4O_2 < \begin{smallmatrix} CO \\ HN \end{smallmatrix} > C_6H_4$ , which crystallises in reddish-yellow needles, and melts above  $400^\circ$ . With orthophenylenediamine it yields a dark yellow *azine*, which melts at  $276^\circ$ , and it can be readily hydrolysed to hydroxynaphthaquinone and anthranilic acid. When suspended in acetic acid and reduced with sulphurous anhydride, it yields brown, crystalline 1 : 2-dihydroxy-3 : 4-naphthacridone,  $C_{10}H_4(OH)_2 < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C_6H_4$ ; this is not, like alizarin, a stable substance, nor does it dye with mordants; it has rather the properties of a quinol-derivative, being oxidisable with extreme readiness to the corresponding quinone; its yellow *diacetyl derivative* melts at  $280^\circ$ .

C. F. B.

**Dihydrophenonaphthacridine and Phenonaphthacridine.** By M. SCHÖPFF (*Ber.*, 1894, **27**, 2840—2845; compare *Abstr.*, 1894, i, 41).—*Dihydrophenonaphthacridine*,  $C_{10}H_6 < \begin{smallmatrix} CH_2 \\ NH \end{smallmatrix} > C_6H_4$ , has been already described as phenonaphthacridine (*loc. cit.*); the *acetyl derivative* melts at  $181-181.5^\circ$ .

*Phenonaphthacridine*,  $C_{10}H_6 < \begin{smallmatrix} CH \\ N \end{smallmatrix} > C_6H_4$ , is obtained by oxidising the dihydro-derivative with silver nitrate; it melts at  $225-226^\circ$ . The *hydrochloride* and the *nitrate* crystallise in dark needles; the *platinochloride* forms minute, violet needles, and the *picrate* separates in brown needles. The *ethyl derivative* crystallises from alcohol in dark needles.

When phenonaphthacridone is reduced with sodium amalgam, the foregoing substance is formed in association with a red substance, which does not melt below  $360^{\circ}$ . If reduction is effected by means of zinc dust and acetic acid, the *hydroxydihydrophenonaphthacridine*,  $C_{10}H_8 < \begin{smallmatrix} CH(OH) \\ NH \end{smallmatrix} > C_6H_4$ , which melts at  $345^{\circ}$ , is formed. It yields brown solutions with sulphuric acid and alcoholic potash, and is not dissolved by aqueous alkali. Reddish-brown fumes are evolved when the substance is heated, and a brown sublimate is formed, exhibiting the violet colour reaction of phenonaphthacridine with sulphuric acid.

M. O. F.

**Analyses of Cotton Dyed with Alizarin.** By C. LIEBERMANN and P. MICHAELIS (*Ber.*, 1894, 27, 3009—3019).—This work was undertaken in order to ascertain whether the theory of dyes advanced by Liebermann (*Abstr.*, 1893, i, 370) is in accord with the facts so far as regards the relative proportions of base and dye present in the cloth. The theory has so far derived no support from the authors' observations.

Technically prepared samples of Turkey red, Bordeaux, and dark madder violet were examined, a detailed description of the analytical methods is given, and the results are tabulated. Specimens of cloth practically identical in appearance may contain totally different compounds; for example, the relative proportions of aluminium and tin in an aluminium-calcium-tin "lake," vary greatly, and the metals do not replace each other in atomic proportions. These results, and the somewhat contradictory analyses of other observers, are probably due to the presence of uncombined mordant in the cloth, which should, therefore, always be dyed to the deepest possible shade before being used for analysis.

J. B. T.

**Some Points in Stereochemistry.** By A. COMBES (*Bull. Soc. Chim.*, 1894, [3], 11, 261—263).—A criticism of Bouveault's recent paper (*Abstr.*, 1894, i, 421). The author disputes (a) the novelty, and (b) the correctness of some of Bouveault's theories as to the relation between rotatory activity, and the constitution and stereoisomerism of cyclic compounds.

L. T. T.

**Action of Camphoric Anhydride on Benzene in Presence of Aluminium Chloride.** By E. BURCKE and C. STABIL (*Compt. rend.*, 1894, 119, 426—428).—The action of camphoric anhydride on benzene in presence of aluminium chloride, yields, as chief product, phenylcamphoric acid (*Abstr.*, 1891, 324), and two others, which the authors have isolated. One of these, *phenylcamphoric anhydride*,  $C_{15}H_{18}O_2$ , is formed in quantity depending on the temperature, and is separated from the acid by means of its greater solubility in benzene. It is a yellowish, syrupy liquid, which does not crystallise even after remaining in a vacuum for three months.

The other product is formed when the action is violent and the substances remain in contact for a long time. It is a diphenyl compound, which has the composition  $C_{22}H_{24}O_2$ , and crystallises in reddish-yellow masses from benzene, in which it dissolves more

readily than phenylcamphoric acid. It may have the constitution  
 $\text{CHPr} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{smallmatrix} > \text{CPh} \cdot \text{COPh}.$  C. H. B.

**Natural Resins.** By M. BAMBERGER (*Monatsh.*, 1894, 15, 505—518; compare Abstr., 1892, 204).—The resin from *Pinus laricio* (Poir), which melts at about 100°, is resolved, on digestion with ether, into an  $\alpha$ -modification (80 per cent.), which is soluble in ether, and a  $\beta$ -modification (20 per cent.), which is insoluble in ether. The  $\alpha$ -resin is a reddish-white, amorphous powder, which is soluble in dilute potash, benzene, and toluene, and dissolves in concentrated sulphuric acid, forming a reddish solution; its methoxyl number is 33. The  $\beta$ -resin is a reddish-white powder, also soluble in dilute potash, but insoluble in benzene and toluene; it has a methoxyl number 62, and gives at first a green, and later a violet, coloration when hydrochloric acid is added to its alcoholic solution. When an excess of potash is added to an alcoholic solution of the  $\alpha$ -resin, or of the crude resin, a colourless, crystalline, potassium compound is formed. A cold aqueous solution of the latter, when treated with hydrochloric acid, gives a powdery precipitate of *pinoresinol*,  $\text{C}_{18}\text{H}_{18}\text{O}_6$ , which gradually separates from its alcoholic solution in drusy masses, melts at 80—90°, contains two methoxyl groups, takes up 2 atoms of iodine, and furnishes the following derivatives.

The *potassium salt*,  $\text{C}_{18}\text{H}_{16}\text{O}_6\text{K}_2 + 4\text{H}_2\text{O}$ , is very soluble in water and methylic alcohol, but is insoluble in ethylic alcohol; the *calcium salt*,  $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Ca}$ , is a white, insoluble precipitate; the *diacetyl-derivative*,  $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Ac}_2$ , crystallises in slender, white needles, and melts at 164°; the *dibenzoyl-derivative*,  $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Bz}_2$ , crystallises in short prisms, and melts at 160°. On treatment with methylic iodide, the potassium salt is converted into *dimethylpinoresinol*,  $\text{C}_{18}\text{H}_{16}\text{O}_6\text{Me}_2$ , which crystallises in scales and melts at 94°. The formula for pinoresinol must, therefore, be  $\text{C}_{18}\text{H}_{10}\text{O}_2(\text{OH})_2(\text{OMe})_2$ . The caffeic and ferulic acids found in an earlier investigation (*loc. cit.*) are, in all probability, present in the resin in an uncombined state. G. T. M.

**Scammony Resin.** By H. SPIRGATIS (*Arch. Pharm.*, 1894, 232, 482—486).—A reply to Poleck (Abstr., 1894, i, 471), maintaining the correctness of his former work, and especially of the analyses and proposed formula of barium scammonate. L. T. T.

**Gaultherin, a New Glucoside from Betula Lenta.** By A. SCHNEEGANS and J. E. GEROCK (*Arch. Pharm.*, 1894, 232, 437—444).—In 1844, W. Procter, jun., announced (*Amer. J. Pharm.*, N.S., 15, 249) the existence, in the bark of *Betula lenta*, of a glucoside, to which he gave the name gaultherin; he did not, however, obtain it in the pure state, and the authors have therefore re-examined the *Betula lenta* bark. In extracting the bark, it was found that even with 94 per cent. alcohol partial hydrolysis of the glucoside took place, the odour of methylic salicylate becoming apparent. By using for extraction a solution of lead acetate (15 per cent. of the weight of the bark) in strong alcohol, this decomposition was pre-

vented. *Gaultherin*,  $C_{14}H_{18}O_8 + H_2O$ , crystallises in colourless needles, which are easily soluble in glacial acetic acid and in alcohol, slowly but freely in water, and almost insoluble in ether, chloroform, benzene, and acetone. The aqueous solution does not affect iron salts, nor does it affect Fehling's solution in the cold, but at  $100^\circ$  cuprous oxide is at once precipitated. Strong sulphuric acid dissolves the glucoside, forming a pale red solution, which rapidly darkens and decomposes. When the dry glucoside is heated, the odour of methylic salicylate becomes apparent at about  $100^\circ$ , and the substance blackens and decomposes at  $120^\circ$ . The aqueous solution has a bitter taste and is levorotatory. The glucoside is decomposed by mineral acids, by alkalis, or by heating the aqueous solution at  $130$ – $140^\circ$ , yielding a carbohydrate and methylic salicylate. L. T. T.

**Crystalline Constituents of True Coto Bark.** By O. HESSE (*Annalen*, 1894, 282, 191–207; compare Abstr., 1894, i, 380).—The coto bark employed by Jobst and Hesse (Abstr., 1880, 325) was derived from Bolivia, whilst nowadays the term has been extended to include varieties from Venezuela and Brazil. The following results were obtained with the bark from Bolivia.

Cotoïn extracted from this bark is identical with that obtained from other varieties. *Benzoylcotoïn* is formed by the direct action of benzoic anhydride, and crystallises in compact lustrous prisms, melting at  $110$ – $112^\circ$ . It gives a brownish-red coloration with ferric chloride. *Dibenzoylcotoïn* is best prepared by the action of benzoic chloride on cotoïn, and crystallises in concentric groups of small needles, melting at  $134$ – $135^\circ$ . Hydrocotoïn only yields one *benzoyl*-derivative, which crystallises in white needles, melts at  $113^\circ$ , and gives no coloration with ferric chloride.

The substance known as dicotoïn has the formula  $C_{25}H_{20}O_6$ , and not  $C_{44}H_{34}O_{11}$  as formerly supposed. The cryoscopic determination of the molecular weight, however, gives the number 214, instead of 416, as required by the above formula. This is explained by the fact that dicotoïn is in reality a mixture of cotoïn with a substance which has the composition and molecular weight corresponding with the formula  $C_{11}H_8O_2$ , and may be obtained from dicotoïn by adding ferric chloride to its alcoholic solution and evaporating. The iron compound of cotoïn is thus formed, whilst the new substance crystallises out in long needles. It separates from light petroleum in colourless, strongly lustrous plates, melts at  $60$ – $61^\circ$ , and volatilises at a higher temperature. It does not contain the hydroxy-group, and gives no coloration with ferric chloride. With phenylhydrazine, it forms a compound of the formula  $C_{23}H_{22}N_4O$ , which crystallises in colourless needles, melting at  $194^\circ$ . In all its properties, it bears a very close resemblance to phenylcoumalin; as, however, the latter melts at  $68^\circ$ , the identity of the two cannot be considered as proved.

Pseudodicotoïn,  $C_{25}H_{20}O_7$ , is also a mixture of cotoïn with a substance of the formula  $C_{11}H_8O_3$ , which the author terms *hydroxyphenylcoumalin*; this crystallises from light petroleum in colourless plates or white needles, and melts at  $61^\circ$ . Acetic anhydride converts it into *acetoxypheylcoumalin*,  $C_{14}H_7AcO_3$ , which crystallises in

lustrous needles and melts at 65°. With phenylhydrazine, it forms a compound,  $C_{23}H_{22}N_4O_2$ , crystallising in flat needles and melting at 193°. When treated with aqueous potash, it is converted into  $\beta$ -phenylcoumalic acid,  $C_{11}H_{10}O_3$ , which crystallises from acetic acid in prisms or plates and melts at 207°. The melting point is, however, uncertain, as the acid passes gradually into its lactone, which melts at 221°.

The paracotoïn obtained from the specimens in question agreed in properties with that previously described. The author confirms the occurrence of piperonylic acid among the products obtained by fusing paracotoïn with potash (Ciamician and Silber, Abstr., 1894, i, 51).

A. H.

### Properties of the Dihydroquinolines, and the Constitution of Ring Systems containing Nitrogen.

By G. CIAMICIAN (*Ber.*, 1894, 27, 3077—3081).—It has already been shown by Ferratini (Abstr., 1893, i, 602) that the trimethyldihydroquinoline obtained by the action of methylic iodide on 2'-methylindole, which has one of the following formulæ,  $C_6H_4 \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ | \\ \text{NMe} \cdot \text{CHMe} \end{smallmatrix}$  or  $C_6H_4 \begin{smallmatrix} \text{CHMe} \cdot \text{CH} \\ | \\ \text{NMe} - \text{CMe} \end{smallmatrix}$  has properties which strongly resemble those of the indoles, although it may be readily converted into quinoline derivatives. The author finds further that when the hydriodide of dihydrotrimethylquinoline is heated, it loses methylic iodide and is converted into trimethylindole, the yield of the latter being very satisfactory. The action is analogous to that which takes place when the hydriodides of tertiary bases are heated, methylic iodide and the corresponding secondary base being obtained.

The great similarity in the properties of the two series is readily explained by the above formulæ of the dihydroquinoline derivatives and the usual formula of the indole ring, the former being "nuclear" homologues of the latter. Bamberger's centric formulæ with a quinquavalent nitrogen atom do not, however, afford a ready explanation of the analogy.

H. G. C.

### Ethereal Salts and Betaines of Quinolinesulphonic acids.

By A. CLAUS and J. STEINITZ (*Annalen*, 1894, 282, 130—138; compare the next abstract).—*Methylic quinoline-1-sulphonate*,



is obtained by the action of methylic iodide on the silver salt at 85°, and crystallises in colourless, lustrous prisms melting at 96°. It gradually decomposes when kept, with formation of the free acid and a volatile oil, which has not yet been analysed; this decomposition proceeds much more rapidly at 100°. The *benzylic salt* crystallises in splendid, six-sided tablets and prisms, which have a diamond lustre, and melt at 84°. When heated at 200°, it decomposes with formation of the free acid and an oil, which has the empirical formula  $C_{14}H_{13}$ . These two salts and the ethylic salt do not appear to form a methiodide, and it has therefore been found impossible to prepare the corresponding betaines.

*Quinoline-4-sulphonic acid methylbettaïne*,  $C_9NH_6MeSO_3$ , is readily formed, and crystallises in yellowish prisms, which can be heated to  $360^\circ$  without undergoing any change. It dissolves in alkalis, but cannot be recovered, either free or in the form of a salt, by acidifying the solution. The bettaïne, moreover, does not combine with allylic iodides.

Similar results were obtained with *quinoline-3-sulphonic acid methylbettaïne*, which may be prepared from the silver salt and methylic iodide at  $100^\circ$ .

The systematic investigation of this action has shown that many of the monobromo-derivatives of the 4- and 3-sulphonic acids only yield ethereal salts when their salts are heated with methylic iodide, whilst others, such as the 3-bromo- and 3-chloro-4-sulphonic acids only yield betaines. A. H.

**Alkyl Derivatives of Quinaldine- $\beta$ -carboxylic acid.** By A. CLAUS and J. STEINITZ (*Annalen*, 1894, **282**, 107—130; compare Abstr., 1893, i, 728). — Ethylic quinaldine- $\beta$ -carboxylate methiodide,  $C_9NH_6Me\cdot COOEt, MeI$ , has been described by Hantzsch (Abstr., 1886, 369). The *methochloride* crystallises in long, colourless needles, melting at  $158^\circ$ . The behaviour of these compounds towards alkalis has already been described by Hantzsch. The authors find that the insoluble amorphous yellow substance finally obtained has the composition  $C_{13}NH_{13}O_2\cdot CH_2$ , but it is probably a polymeride.

*Ethylic quinaldinecarboxylate ethiodide* is formed with considerable difficulty, and crystallises in groups of plates which melt and decompose at  $236^\circ$ . The *ethochloride* forms well-developed prisms, and melts at  $146^\circ$ ; its *platinochloride*,  $(C_{13}H_{13}O_2N, EtCl)_2PtCl_4$ , crystallises in compact, red prisms, and melts and decomposes at  $238^\circ$ .

*Ethylic ethylidenequinaldinium- $\beta$ -carboxylate*,  $C_{13}NH_{13}O_2\cdot CHMe$ , is obtained as an amorphous, yellowish-red mass, which has not been analysed, by the action of alkalis on the ethiodide. It is completely soluble in ether, and does not undergo polymerisation to an insoluble compound when kept. On treatment with hydrochloric acid, it yields the *ethochloride* melting at  $146^\circ$ . The *silver salt* of quinaldine- $\beta$ -carboxylic acid is a micro-crystalline powder, and when treated with methylic iodide yields the *methylic salt* of the acid. This substance can also be obtained by synthesis from methylic acetoacetate and orthamidobenzaldehyde, and by the action of methylic iodide on quinaldinecarboxylic acid; in the latter case, the direct product is the hydriodide of the methylic salt. The methylic salt forms colourless needles, melting at  $72^\circ$ .

The following additive compounds and ethereal salts of quinaldine- $\beta$ -carboxylic acid have also been prepared. From the methylic salt, the *methiodide*, vitreous, yellow prisms, melting at  $200^\circ$ ; the *methochloride*, colourless, vitreous prisms, melting at  $157^\circ$ ; the *ethiodide*, lemon-yellow plates, melting at  $210^\circ$ ; the *ethochloride*, colourless, vitreous needles, melting at  $150^\circ$ ; and the *ethobromide*, granular crystals, melting at  $154^\circ$ . From the ethylic salt, the *ethobromide*, granular crystals, melting at  $217^\circ$ . The *propylic salt* forms colourless,

vitreous prisms, and melts at  $51^{\circ}$ ; the *propylic methiodide* golden-yellow needles, melting at  $186^{\circ}$ ; the *benzylic salt* forms colourless prisms, melting at  $82^{\circ}$ , and the *benzylic methiodide* flat, golden-yellow needles, melting at  $172^{\circ}$ .

The methylic methochloride and iodide, when treated with alkalis, yield a yellow, amorphous substance which behaves in a similar manner to the corresponding derivative of the ethylic salt. It is a yellow powder, melts and decomposes at  $182^{\circ}$ , and has the formula of *methylic methylenequinaldinium- $\beta$ -carboxylate*,



of which it is probably a polymeride.

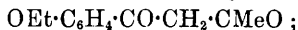
Quinaldine- $\beta$ -carboxylic acid differs from the  $\gamma$ -carboxylic acids of the quinoline series in two important respects. It forms no direct additive compounds with halogen alkyls without at the same time being converted into an ethereal salt, and the additive compounds of the ethereal salts do not yield the corresponding betaine when treated with alkalis.

*Quinaldine- $\beta$ -carboxylic acid methochloride* can, however, be readily obtained by heating the methochloride of one of the ethereal salts with fuming hydrochloric acid. It forms short, vitreous prisms, and melts with decomposition at  $230^{\circ}$ . The corresponding *betaine* forms thick, monosymmetric prisms containing  $2\text{H}_2\text{O}$ , which are lost at  $100^{\circ}$ , the anhydrous compound melting at  $144^{\circ}$ . It has an intensely bitter taste, and is readily decomposed with formation of a violet colouring matter. It unites readily with methylic and ethylic iodides to form compounds which are in every respect identical with the methylic methiodide and ethylic methiodide already described. This behaviour confirms the view expressed by Claus and Büttner (Abstr., 1893, i, 731) as to the course of the analogous reaction with  $\alpha$ -phenyl-cinchoninic acid.

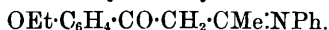
The betaine dissolves in alkalis, forming a salt which could not be isolated, and does not form an oxinic acid.

A. H.

**4'-Orthohydroxyphenylquinoline and 4'-Metahydroxyphenylquinoline.** By E. BESTHORN, E. BANZHAF, and G. JAEGLÉ (Ber., 1894, 27, 3035—3043).—*Orthoethoxyacetophenone* was prepared from ethylic ethylsalicylate by Tahara's method (Abstr., 1892, 844); it melts at  $43^{\circ}$ , and boils at  $243$ — $244^{\circ}$ . It was converted, by the same method as that used in the case of the para-compound (Abstr., 1894, i, 344), into *orthoethoxybenzoylacetone*,



this melts at  $58^{\circ}$ , and forms a *sodium salt*, which, when warmed with aniline and acetic acid, yields a yellow *anilide*,



When the latter is heated at  $50^{\circ}$  with sulphuric acid monohydrate, several reactions take place, and as a result of one of these some 4'-*orthoethoxyphenylquinaldinesulphonic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4(\text{SO}_3\text{H})\cdot\text{C}_{10}\text{NH}_8$ , is formed, and crystallises in tiny, white needles. When this is boiled with hydrobromic acid, it is converted into 4'-*orthohydroxyphenyl-*

*quinaldine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_{10}\text{H}_8\text{N}$ , which melts at about  $187\text{--}188^\circ$ ; and its sodium salt. when heated with benzaldehyde and zinc chloride at  $200^\circ$ , yields a *benzylidene compound*,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{C}_{10}\text{H}_8\text{N}\cdot\text{CHPh}$ . If the latter is oxidised with permanganate, and the product heated with hydrobromic acid, yellowish-red 4'-*ortho*hydroxyphenylquinaldinic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}$ , is formed; this melts and decomposes at  $243\text{--}245^\circ$ , and, when heated at  $250^\circ$ , yields 4'-*ortho*hydroxyphenylquinoline,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_9\text{NH}_6$ , identical with the "quinolinephenol" obtained by Koenigs from apocinchene (Abstr., 1893, i, 377).

*Metamethoxyacetophenone* was prepared like the para-compound (Abstr., 1894, i, 344); it boils at  $239\text{--}241^\circ$ . *Metamethoxybenzoylacetone* was obtained as an oil, its *anilide* as yellow needles melting at  $84\text{--}85^\circ$ . This anilide yields a sulphonic acid, the barium salt of which forms a *benzylidene compound*. From the latter 4'-*meta*hydroxyphenylquinaldinic acid can be obtained; this melts and decomposes at about  $235^\circ$ , yielding 4'-*meta*hydroxyphenylquinoline, identical with the Py-3- $\beta$ -phenolquinoline of Koenigs and Nef (Abstr., 1887, 599).

C. F. B.

**Paramethoxy- $\alpha$ -phenylcinchoninic acid, Parahydroxycinchoninic acid, and Parahydroxy- $\alpha$ -phenylcinchonine.** By A. CLAUS and G. BRANDT (*Annalen*, 1894, **282**, 85—107).—3-Methoxy-2'-phenylcinchoninic acid *methiodide*,  $\text{OMe}\cdot\text{C}_9\text{NH}_4\text{Ph}\cdot\text{COOH}\cdot\text{MeI}$ , is obtained by heating  $\alpha$ -phenylquininic acid with methylic iodide at  $135\text{--}136^\circ$ , and forms aggregates of small, reddish-yellow needles, melting at  $216^\circ$ . The *methochloride* is prepared by triturating the *methiodide* with moist silver chloride, and is a hygroscopic mass, which crystallises from alcohol in small needles, melting at  $195^\circ$ . The corresponding *betaine* is formed when the *methiodide* is treated with moist silver oxide, and crystallises with  $\text{H}_2\text{O}$  in yellow, vitreous prisms, which become anhydrous at  $100^\circ$  and melt at  $218^\circ$ . The *betaine* is also formed when the aqueous solutions of the *methochloride* and *iodide* are boiled, and when these substances are treated with alkalis. The further action of alkali produces a quaternary ammonium hydroxide of the formula  $\text{OMe}\cdot\text{C}_9\text{NH}_4\text{Ph}\cdot\text{COOH}\cdot\text{MeOH}$ , from which the original *betaine*, or one of its salts, can readily be regained by acidification of its solution. This substance, probably owing to the presence of the phenylic group, is much more stable than the corresponding derivative of quininic or cinchoninic acid, and does not form an oxinic acid.

It was found impossible to prepare an ethobromide of the acid. The *sodium salt* of methoxyphenylcinchoninic acid forms slender, yellow needles, containing  $6\text{H}_2\text{O}$ , whilst the *copper salt* is a light green precipitate. The *hydrochloride*,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N} + 3\text{HCl}$ , crystallises from concentrated hydrochloric acid in lemon-yellow, vitreous needles, and loses  $2\text{HCl}$  at  $100^\circ$ .

3-Hydroxycinchoninic acid *methiodide*,  $\text{OH}\cdot\text{C}_9\text{NH}_5\cdot\text{COOH}\cdot\text{MeI}$ , is formed from its components with considerable difficulty, and crystallises from alcohol in splendid, orange-yellow, vitreous prisms, melting at  $302^\circ$ . Its solution in water readily decomposes, with formation of resinous compounds. The *methochloride* may be prepared by the action of silver chloride, but is best obtained by heating



the methochloride of quinic acid with fuming hydrochloric acid at 230°, this being a reaction capable of general application to this class of substances. It forms flat, green crystals, and melts at 295°. The corresponding *betaine* is formed by the action of water, alkalis, or silver oxide on the foregoing compounds, and crystallises with 1H<sub>2</sub>O in large tablets or prisms, which lose their water at 100° and melt at 304°. The product of the action of alkalis on the betaine, *methyloquinoliniumhydroxidecarboxylic acid*, has not been isolated. Its solution is stable in the air, so that the presence of the free hydroxy-group has the same influence on the stability of the compound as has the phenylic group in the case of methoxyphenylcinchoninic acid.

*3-Hydroxy-2'-phenylcinchoninic acid*, OH·C<sub>6</sub>H<sub>4</sub>·Ph·COOH, may be prepared, by Döbner's method, from parahydroxyaniline, pyruvic acid, and benzaldehyde, and forms small, vitreous plates and needles, which decompose at 295—300°. Its alkaline solutions become dark brown on exposure to the air. The *copper* and *silver* salts are amorphous precipitates. The *methochloride* is prepared by the action of hydrochloric acid at 230—235° on the methochloride of methoxyphenylcinchoninic acid, and forms greenish-yellow, lustrous plates, melting at 248°. The *methiodide* can only be obtained with great difficulty from its components and is very unstable. The *betaine* forms almost colourless, granular crystals, and melts at 243°. The alkaline solutions of the betaine are somewhat unstable, but no compound of the nature of an oxinic acid is formed, resinous matter being gradually produced.

The solubility of the substituted cinchoninic acids is shown in the following table. 100 grams of the boiling saturated solution contains

Paramethoxycinchoninic acid .....	1.24 grams.
Paramethoxy- $\alpha$ -phenylcinchoninic acid ...	2.22 „
Parahydroxycinchoninic acid.....	0.28 gram.
Parahydroxy- $\alpha$ -phenylcinchoninic acid ...	0.44 „

A number of ethereal salts have also been prepared by the action of an alkyl iodide on the silver salt of the acid.

	Methylic salts.	Ethylic salt.
	M. p.	M. p.
2'-Phenylcinchoninic acid .....	61°	—
3-Methoxycinchoninic acid .....	85	—
3-Methoxy-2'-phenylcinchoninic acid ..	111	105°
3-Hydroxy-2'-phenylcinchoninic acid ..	148	—

These salts readily undergo decomposition when heated, the free acid being formed, together with a terpene-like substance, the nature of which has not yet been determined. A. H

**Pure Dextrorotatory Coniine.** By A. LADENBURG (*Ber.*, 1894, 27, 3063—3066).—Coniine was prepared synthetically in the same way as before, but on a larger scale; 30 grams of inactive coniine, boiling at 165—169°, were obtained. This was treated with dextro-

rotatory tartaric acid, as before, when the salt of dextrorotatory coniine crystallised out. This was, however, now recrystallised three times, after which it yielded a coniine, boiling at  $167.7^{\circ}$  (corr.), and with sp. gr. = 0.8438 and specific rotation  $[\alpha]_D = +18.3^{\circ}$ , both at  $23^{\circ}$ . The difference between this and the earlier numbers is attributed to the presence of isoconiine in the sample then investigated.

C. F. B.

**Nicotine (Metan nicotine).** By A. PINNER (*Ber.*, 1894, **27**, 2861—2869; compare *Abstr.*, 1894, i, 388).—When the additive compound of benzoic chloride and nicotine is heated with strong hydrochloric acid at  $100^{\circ}$ , benzoic acid and nicotine are formed, whilst, if boiled with sodium ethoxide, hydrogen chloride is eliminated and benzoyl-metan nicotine is produced. *Acetylmotan nicotine* is obtained by heating nicotine with acetic anhydride for 10—12 hours at  $170^{\circ}$ ; it is hydrolysed only with difficulty, yielding metan nicotine. When metan nicotine is heated with a strong solution of barium hydroxide for 10—12 hours at  $170^{\circ}$ , methylamine is formed, together with a base,  $C_8H_9N$ , of which the *picrate* melts at  $151^{\circ}$ .

The action of bromine on metan nicotine gives rise to the compound,  $C_{10}H_{14}Br_2N_2 \cdot 2HBr \cdot Br_2$ , crystallising in reddish-yellow needles, which melt at  $170^{\circ}$ . On adding dilute caustic soda to the hydrobromide of metan nicotine bromide, *monobromometan nicotine*,  $C_{10}H_{13}BrN_2$ , separates in the form of an oil; the *picrate* melts at  $190^{\circ}$ . Reduction with hydrochloric acid and zinc dust gives rise to the formation of metan nicotine.

The optical activity of cotinine, dibromocotinine, and dibromoticonine has been determined. The first-named has  $[\alpha]_D = -56^{\circ}$ , whilst dibromocotinine has  $[\alpha]_D = +95.5^{\circ}$ , and dibromoticonine has  $[\alpha]_D = +13.6^{\circ}$ ; the determinations were made at  $20^{\circ}$ .

M. O. F.

**Derivatives of Caffeine.** By L. CRÄMER (*Ber.*, 1894, **27**, 3089—3092).—*Methylamidocaffeine*,  $C_8H_9N_4O_2 \cdot NHMe$ , is readily obtained in a similar manner to amidocaffeine by heating chlorocaffeine with methylamine and alcohol at  $100^{\circ}$ ; it crystallises from hot water in slender, colourless needles, melts at  $310$ — $315^{\circ}$ , simultaneously becoming brown. The *picrate* crystallises in yellow plates. *Ethylamidocaffeine*,  $C_8H_9N_4O_2 \cdot NHEt$ , is prepared in a similar manner, and also forms slender needles, melting at  $226$ — $230^{\circ}$  with partial sublimation.

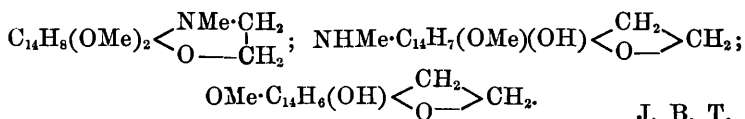
*Hydrazidocaffeine*,  $C_8H_9N_4O_2 \cdot N_2H_3$ , prepared by boiling chlorocaffeine with an aqueous solution of hydrazine hydrate, crystallises in slender, colourless needles, melting and completely decomposing at  $240^{\circ}$ . It reduces Fehling's solution on warming, and yields a *hydrochloride*, which crystallises well and dissolves readily in warm water. With benzaldehyde, the hydrazine compound forms *benzylidenehydrazidocaffeine*,  $C_8H_9N_4O_2 \cdot N_2H \cdot CHPh$ ; this crystallises in slender needles, melting at  $270^{\circ}$  to a brown liquid. On treatment with nitrous acid, it is converted into *azimidocaffeine*,  $C_8H_9N_4O_2N_3$ , which forms colourless needles, sparingly soluble in water, and rapidly becomes red in the air when moist.

*Anilidocaffeine*,  $C_8H_9N_4O_2 \cdot NHPh$ , crystallises from alcohol in colour-

less needles, melting at about  $260^{\circ}$  and decomposing at a slightly higher temperature; the *hydrochloride*,  $C_{14}H_{15}N_5O_2 \cdot HCl$ , also crystallises in needles, which are dissociated by water. *Nitrosoanilidocaffeine*,  $C_8N_4H_9O_2 \cdot NPh \cdot NO$ , decomposes at about  $225^{\circ}$  and gives Liebermann's reaction. *Benzoylanilidocaffeine*,  $C_8N_4H_9O_2 \cdot NPhBz$ , is obtained by boiling anilidocaffeine with benzoic chloride, and, after crystallisation from alcohol, melts at  $225^{\circ}$ . By the action of alcoholic potash on anilidocaffeine at  $120^{\circ}$ , it is converted into *anilidocaffedine*, the sulphate of which crystallises well; the action of hydrochloric acid and potassium chlorate converts it into chloranil and dimethylalloxan. *Paratoluidocaffeine* melts at  $270-275^{\circ}$ , *orthotoluidocaffeine* at  $230^{\circ}$ , and *metaxylicocaffeine* at  $210-212^{\circ}$ . H. G. C.

**Thebaine.** By M. FREUND (*Ber.*, 1894, **27**, 2961—2963).—Thebenine is not isomeric with thebaine as Hesse thought, but contains hydroxyl in place of methoxyl, its *methiodide*,  $C_{20}H_{24}NO_3I$ , is crystalline, melts at  $210^{\circ}$ , and is resolved into trimethylamine and *thebenol*,  $C_{17}H_{14}O$ , on fusion with alkalis. Thebenol melts at  $186^{\circ}$ , and by distillation with zinc dust, or reduction with hydriodic acid and phosphorus, yields a hydrocarbon which melts at  $135^{\circ}$ , and is perhaps an ethylphenanthrene.

*Thebenine ethiodide* when fused with alkalis yields thebenol and methyl-diethylamine, proving that thebenine is a secondary base. Thebaine is a tertiary base, but its relationship to thebenine precludes the presence in it of the group  $NMe_2$ . When treated with alkalis, its methiodide yields tetramethylethylenediamine, not trimethylamine, as Roser stated; it is probable that dimethylhydroxyethylamine, which is closely related to morphine, is formed as intermediate product. The production of the ethylene base resembles that of tetraethylethylenediamine from triethylaminethylene iodide as observed by Ladenburg. The following provisional formulæ are given for thebaine, thebenine, and thebenol respectively



J. B. T.

**Opium Alkaloids.** By O. HESSE (*Annalen*, 1894, **282**, 208—214).—When crude laudanine (*Annalen*, Suppl.-Bd., **8**, 272) is converted into the hydrochloride and this is recrystallised from water, the mother liquor is found to contain an alkaloid, *laudanidine*,  $C_{20}H_{25}NO_4$ , which is isomeric with laudanine, but differs from it in being optically active ( $[\alpha]_D = -87.8^{\circ}$ ). The new alkaloid melts at  $177^{\circ}$  (laudanine melts at  $166^{\circ}$ ), but in other properties closely resembles its isomeride. The *hydrochloride* is much more readily soluble in water than that of laudanine. The *hydriodide* is sparingly soluble, and the *platinochloride* is a brownish-yellow, amorphous mass. The *hydrogen oxalate* forms small, white needles. Acetic anhydride converts it into *acetyl-laudanidine*, which crystallises with  $1H_2O$ , melts at about  $98^{\circ}$ , and dissolves in dilute aqueous potash and soda, but not in ammonia. It

seems probable that laudanine consists of two optically opposed constituents, of which laudanidine is one, but this question is being further investigated. A. H.

**Benzoylquinine.** By A. WUNSCH (*Compt. rend.*, 1894, **119**, 407—409).—Schützenberger obtained benzoylquinine by the action of benzoic chloride on the alkaloid, and described it as a resinous and uncrystallisable substance. The author prepares it by adding gradually, with frequent agitation, 60 parts of pure, well-dried, and finely-powdered quinine to 100 parts of benzoic chloride, heated on a water bath. The product, after cooling, is treated with several times its volume of cold water, which rapidly dissolves the benzoylquinine hydrochloride, but only very slowly attacks the excess of benzoic chloride. The base is purified by precipitation with ammonia and crystallisation from aqueous ether. It forms very distinct, highly refractive, colourless prisms of the composition



Benzoylquinine is insoluble in water, and the crystals remain unchanged even in contact with boiling water, but it dissolves readily in alcohol, benzene, chloroform, light petroleum, and carbon bisulphide, and also in ether, especially if it contains water. It crystallises from all the solvents except alcohol, and the crystals, which are anhydrous, melt at  $139^\circ$ , but decompose at a higher temperature.

Benzoylquinine is distinguished from quinine benzoate by its insolubility in water and its resistance to the action of potassium hydroxide. Like quinine, it yields a green coloration with chlorine water and ammonia, and the dilute aqueous solutions of its salts are fluorescent. It is neutral to both phenolphthaleïn and litmus, and even the basic salts are acid to litmus.

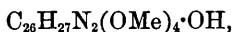
It forms two series of salts, namely, *basic salts*, which contain 1 mol. of the base and 1 mol. of a monobasic acid, and *normal salts*, which contain twice as much acid. The basic salts are very stable, and are insoluble, or almost insoluble, in water. They are usually hydrated, and effloresce rapidly. The normal salts are partially decomposed by water. The *basic hydrochloride* crystallises from alcohol in acicular prisms containing  $\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ , and is very soluble in alcohol; the *normal hydrochloride* crystallises from absolute alcohol in small, square prisms, which contain 1 mol.  $\text{EtOH}$ , absorb moisture rapidly from the air, and dissolve in all proportions in water and alcohol. The *basic salicylate* crystallises from dilute alcohol in anhydrous lamellæ; the *basic tartrate* forms brilliant needles containing  $9\text{H}_2\text{O}$ ; the *basic succinate* forms colourless prisms, which contain  $8\text{H}_2\text{O}$ , and effloresce very rapidly. C. H. B.

**Emetine.** By H. KUNZ-KRAUSE (*Arch. Pharm.*, 1894, **232**, 466—481).—This paper is a continuation of the author's previous work (H. Kunz, *Abstr.*, 1887, 980). Methylemetonium hydroxide (*loc. cit.*) has now been obtained as a golden-yellow, amorphous powder. Its solution is very strongly alkaline, and absorbs carbonic anhydride

from the air. The *carbonate* is an amorphous powder, softening at  $120^{\circ}$ , and melting with evolution of carbonic anhydride at  $156-160^{\circ}$ . *Ethylemetonium iodide*,  $C_{30}H_{40}N_2O_5EtI$ , crystallises in white needles; the *hydroxide* resembles the methyl base. Both these derivatives are quaternary ammonium bases.

In the preparation of emetine, a *colour base*, containing both nitrogen and sulphur, was found among the residues. The authors believe this to be an acetyl derivative of emetine, and by heating emetine with other acids, and with acetic and benzoic anhydrides, &c., they have obtained derivatives apparently analogous to it. This reaction is being further studied.

When emetine is heated with hydriodic acid, 4 mols. of methylic iodide are eliminated. Emetine therefore contains four methoxyl groups and almost certainly one hydroxyl group. The constitution of emetine may, therefore, be represented by the formula



and the nucleus  $C_{26}H_{27}N$  probably contains one or more tertiary butyl-toluene groups.

The author maintains the correctness of the above formula against Paul and Cownley's contention (*Abstr.*, 1894, i, 155, and *Pharm. J. Trans.*, 1894, [3], 54, 111), that emetine is a mixture of two alkaloids,  $C_{15}H_{22}NO_2$  and  $C_{11}H_{20}NO_2$ , and calls attention to the fact that each of these formulæ contains an uneven number of valencies.

Both methylemetine and the colour base resemble curare in their physiological action, producing paralysis of the motory system and then death.

L. T. T.

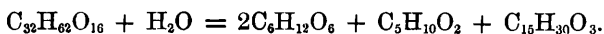
**Identity of Cytisine and Ulexine.** By A. PARTHEIL (*Arch. Pharm.*, 232, 486-488).—The author maintains his claim to priority in proving the identity of these two alkaloids.

**The Products of Hydrolysis of Convolvulin, and its Composition.** By H. J. TAVERNE (*Rec. Trav. Chim.*, 1894, 13, 187-217).—Convolvulin, extracted by alcohol from jalap-root coming from Vera Cruz, was hydrolysed by dissolving it in baryta water, removing the barium with sulphuric acid, and boiling the solution with  $\frac{1}{2}$  per cent. of free sulphuric acid. There were formed a volatile acid (methylethylacetic), a crystalline acid (hydroxypentadecylic) not volatile with steam, and a sugar which could not be obtained in the crystalline form, but which the author is nevertheless inclined to regard as glucose.

*Methylethylacetic acid*,  $CHMeEt\cdot COOH$ , is identical with the substance obtained by Pagenstecher (*Abstr.*, 1879, 455), except that it is optically active, having specific rotation  $[\alpha]_D = +17^{\circ} 30'$ . *Hydroxypentadecylic acid*,  $CHMeEt\cdot CH(OH)\cdot C_9H_{18}\cdot COOH$ , melts at  $50.5^{\circ}$  when pure; its *methylic salt* melts at  $35^{\circ}$ , and boils at  $206-208^{\circ}$  under 15 mm. pressure. When it is heated with phosphorus pentachloride and the product reduced with hydriodic acid and phosphorus, a *pentadecylic acid*,  $C_{15}H_{30}O_2$ , is obtained; this melts at  $48^{\circ}$ , and is isomeric, therefore, with the normal acid, which melts at  $51^{\circ}$ ; it boils at  $206^{\circ}$

under 14 mm. pressure. When the hydroxy-acid is oxidised with nitric acid, it yields methylethylacetic acid, and an acid,  $C_{10}H_{18}O_4$ , which melts at  $116^\circ$ , and boils at  $235^\circ$  under 13 mm., and at  $294^\circ$  under 100 mm. pressure; this acid is isomeric with sebacic acid, which melts at  $133-133.5^\circ$

Possibly, convolvulin has the formula  $C_{32}H_{62}O_{16}$ , and its hydrolysis may then be represented by the equation



C. F. B.

**Two Cactus Alkaloids.** By A. HEFFTER (*Ber.*, 1894, 27, 2975—2979).—*Anhaline*,  $C_{10}H_{17}NO$ , is extracted from *Anhalonium fissuratum*; it crystallises in colourless, stellate prisms, and melts at  $115^\circ$ . The solution in concentrated sulphuric acid is colourless, even when warmed, but becomes green on the addition of a drop of nitric acid. The most characteristic reaction is the production of a yellow colour with nitric acid, changing to orange-red with potash. The *sulphate*,  $(C_{10}H_{17}NO)_2 \cdot H_2SO_4 + 2H_2O$ , crystallises in colourless, lustrous plates, and melts at  $197^\circ$ . The *hydrochloride*,  $C_{10}H_{17}NO \cdot HCl$ , crystallises in slender, hygroscopic plates. The *oxalate* is anhydrous and resembles the sulphate. The yield of alkaloid was very small, only 0.2 gram from 1 kilo. of the dry plant.

*Pellotine*,  $C_{13}H_{21}NO_3$ , so called from the Mexican name "pellote," of *Anhalonium Williamsi*, crystallises in colourless, transparent, anhydrous plates, and melts at  $110^\circ$ . The yield is 0.89 per cent. of the fresh plant. It dissolves in sulphuric acid with a slight yellow colour, changing to deep red with nitric acid. The *phosphotungstate* and *phosphomolybdate* are voluminous, the former white, the latter lemon coloured. The *potassiomericcuric iodide* crystallises in pale yellow prisms; the *potassiocadmium iodide* in colourless, rectangular plates; the *potassiobismuth iodide* is amorphous at first, but changes to needles; the *iodopotassium iodide* crystallises in slender needles. The *picrate* crystallises in stellate prisms. The *platinochloride* is deposited in golden-yellow crystals; the *hydrochloride*,  $C_{13}H_{21}NO_3 \cdot HCl$ , in rhombic prisms. The *oxalate* crystallises in needles. The *methiodide*,  $C_{13}H_{21}NO_3 \cdot MeI + H_2O$ , is deposited in colourless prisms melting at  $198^\circ$ . The *methochloride*,  $C_{13}H_{21}NO_3 \cdot MeCl$ , crystallises in slender, colourless needles melting at  $226^\circ$ . Determinations by Zeisel's method show that pellotine contains two methoxy-groups. By the action of hydrochloric acid at  $100^\circ$ , methylic chloride is eliminated and a base formed in small quantity, which yields a *platinochloride* crystallising in orange-red prisms.

J. B. T.

## Organic Chemistry.

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**Action of Reducing Agents on Metallic Cyanides: Compounds of Organic Bases with certain Metallic Salts.** By F. REITZENSTEIN (*Annalen*, 1894, **282**, 267—280).—The author has investigated the red coloration which is developed on immersing a strip of zinc into a solution of potassium nickelocyanide containing ammonia and ammonium chloride (compare Moore, *Abstr.*, 1894, i, 102); he has not, however, arrived at a definite result as to its nature. The coloration is produced when a solution containing only nickelous cyanide is subjected to similar treatment, but it is destroyed on shaking the solution with air. Both potassium nickelocyanide and solid nickelous cyanide, when warmed with alkaline hydroxylamine solution, give a red coloration which does not disappear on shaking; this coloration is not, however, produced in presence of excess of potassium cyanide; indeed, the addition of excess of that reagent decolorises the liquid. As Moore has observed, sodium amalgam readily reduces potassium nickelocyanide, the coloration which is produced rapidly vanishes, however, when the liquid is shaken. Alkali cyanide compounds of cobalt, platinum and zinc give no coloration with zinc dust, sodium amalgam, or hydroxylamine, but with alkaline solutions of hydroxylamine, alkali manganocyanides give a red coloration which is not destroyed by excess of potassium cyanide. When the red solution obtained by heating potassium nickelocyanide with alkaline hydroxylamine is shaken with pyridine, the colouring matter is taken up by the latter; if the pyridine solution is evaporated to a small volume, filtered from potassium chloride, and, after the lapse of some time, the unaltered potassium nickelocyanide is removed, it is found to have the property of reducing solutions of mercuric and silver salts, and to give a bright blue precipitate with hydrochloric acid. When the solution is evaporated to complete dryness, and again taken up with pyridine, a deep blue liquid is formed, from which, on the addition of water, an ultramarine-blue compound separates, which is insoluble in water, alcohol, ether, chloroform, &c., and becomes paler on keeping.

The author then enters into a theoretical discussion on the compounds of ammonia and organic bases with certain metallic salts, and he gives bibliographical references relating thereto. According to the constitutional formulæ proposed by Werner (*Zeit. anorg. Chem.*, **3**, 267) and by Jörgensen, stereoisomerides should exist of the compounds  $RCl_2 \cdot 2C_5NH_5$  ( $R$  = a metallic element), but the author has failed to observe them.

*Dipyridine cobaltous chloride*,  $CoCl_2 \cdot 2C_5NH_5$ , is obtained when the calculated amount of pyridine is added to solid hydrated cobaltous chloride, and the mixture boiled with alcohol; it crystallises from alcohol in bluish needles, becomes darker at  $120^\circ$ , and melts at  $192^\circ$ . Its aqueous solution is red, and the chlorine is quantitatively precipitated therefrom on addition of silver nitrate; it gives the following

reactions :—With potassium cyanide, a greenish-yellow precipitate soluble in excess ; with sodium platonic chloride (warmed), a yellow crystalline precipitate ; with potassium ferrocyanide, an emerald-green precipitate ; with potassium ferricyanide, a bluish-green precipitate. The compound loses pyridine and becomes red if exposed to the air, and when heated at  $106^{\circ}$  it becomes bright blue with the loss of pyridine (1 mol.).

Tetrapyridine cobaltous chloride,  $\text{CoCl}_2 \cdot 4\text{C}_5\text{NH}_5$ , is obtained by treating anhydrous cobaltous chloride with more than six molecular proportions of pyridine, and subsequently boiling ; the compound, after being recrystallised from pyridine, is peach-red ; it becomes blue at  $70^{\circ}$ , partially melts at  $124^{\circ}$ , and fuses complete at  $192$ – $195^{\circ}$  (the melting points of dipyridine cobaltous chloride).

Dipyridine nickelous chloride,  $\text{NiCl}_2 \cdot 2\text{C}_5\text{NH}_5$ , crystallises from alcohol in yellowish, felted needles.

*Diquinoline cobaltous chloride*,  $\text{CoCl}_2 \cdot 2\text{C}_9\text{NH}_7$ , is obtained when quinoline, in excess or otherwise, is added to hydrated cobaltous chloride ; it separates from alcohol in blue crystals, commences to sinter at  $150^{\circ}$ , and melts at  $192$ – $200^{\circ}$ . When boiled with water, a red solution is obtained which exhibits the following reactions :—With mercuric chloride or silver nitrate, white precipitates ; with copper chloride, a greenish precipitate ; with sodium platonic chloride, a yellow, crystalline precipitate ; with hydrochloric acid, a yellow precipitate ; with potassium dichromate, a yellow precipitate soluble in excess ; with iodine and potassium iodide, a reddish-brown precipitate soluble in hydrochloric acid.

When anhydrous cobaltous chloride is heated with an excess of quinoline, a mixture of blue and red crystals separates on cooling ; if these are boiled with a mixture of alcohol and quinoline, and subsequently with alcohol alone, a blue compound, *pentaquinoline dicobaltous chloride*,  $2\text{CoCl}_2 \cdot 5\text{C}_9\text{NH}_7 + \text{H}_2\text{O}$ , remains ; it melts at  $178^{\circ}$ . From the quinoline alcoholic extract, *tetraquinoline cobaltous chloride*,  $\text{CoCl}_2 \cdot 4\text{C}_9\text{NH}_7$ , a red compound, separates ; it is purified by washing with water. It becomes blue at  $125^{\circ}$ , and melts at  $155$ – $158^{\circ}$  ; if heated for several hours at  $106^{\circ}$ , it loses 2 mols. of quinoline, forming *diquinoline cobaltous chloride*,  $\text{CoCl}_2 \cdot 2\text{C}_9\text{NH}_7$ , which melts at  $192$ – $195^{\circ}$ .

A. R. L.

**Ethane and Propane. A Correction.** By K. OLSZEWSKI (*Ber.*, 1894, 27, 3305–3306).—Referring to L. Meyer and Hainlen's recent papers on this subject (this vol., i, 1), the author states that five years ago he experimented with liquid ethane and propane (*Abhand. Krakau. Akad. Wiss.*, 1889). Both substances were purified by repeated distillation at low temperatures. Ethane boils at  $-93^{\circ}$  (1 atmos.) ; the critical temperature is  $34^{\circ}$ , under the critical pressure of 50.2 atmos. Propane boils at  $-45^{\circ}$  (1 atmos.) ; the critical temperature is  $97^{\circ}$ , under the critical pressure of 44 atmos. Both compounds remain liquid at  $-151^{\circ}$ . The vapour pressures at other temperatures are given, and seem to be in accord with those of Meyer and Hainlen at neighbouring temperatures.

J. B. T.



**Carbon Tetriodide, Tetrabromide, and Tetrachloride.** By ROBINEAU and ROLLIN (*Chem. Centr.*, 1894, i, 1140—1141; from *Mon. Sci.*, **13**, 341—342).—Carbon tetriodide is obtained by heating a solution of potassium iodide (10 grams), 25 c.c. of soda of 36° B., and 100 c.c. of water at 80—90°, and then adding 1 c.c. of acetone and 50 c.c. of a 45 per cent. solution of sodium hypochlorite. The carbon tetriodide is obtained in red flocks; it crystallises from chloroform in red octahedra, is decomposed by fuming nitric acid, and reduced by sodium hyposulphite.

Carbon tetrabromide is obtained in white flocks on adding to a strongly alkaline solution of sodium hypobromite, heated at 70—80°, acetone in quantity insufficient to decolorise the mixture. If an excess of acetone is used, bromoform is obtained. The tetrabromide is also obtained on treating a hot solution of a hypochlorite with an alkaline solution of potassium bromide and a little acetone.

Carbon tetrachloride is formed by the action of sodium hypochlorite and soda heated at 60—70° on chloroform. A better result is obtained by employing 2,000 parts of sodium hypochlorite of 45 per cent., 200 parts of soda of 36° B., and 16 parts of acetone, and heating the mixture in a reflux apparatus for three hours. When too much acetone is employed, a mixture of chloroform and the tetrachloride is obtained. Carbon tetrachloride is characterised by its boiling point, vapour density, and smell, its indifference to soda when heated in a sealed tube, and its insolubility in a saturated aqueous solution of carbon tetrachloride. Carbon tetrachloride may be detected in chloroform as follows:—1 c.c. of the sample of chloroform is heated in a sealed tube at 100°, together with 10 c.c. of soda of 36° B. and 10 c.c. of water; if the sample contains tetrachloride, oily drops are formed on cooling the mixture. By this means 1 per cent. of tetrachloride is easily detected. Another method is to shake 1 c.c. of the sample of chloroform with 400 c.c. of a saturated aqueous solution of the tetrachloride, when, if tetrachloride is present in the sample of chloroform, a turbidity is produced. 0.1 per cent. of tetrachloride may be detected by the latter method. E. C. R.

**Sodium and Potassium Nitromethane.** By N. ZELINSKY (*Ber.*, 1894, **27**, 3406—3407).—These salts explode very readily, and attention is drawn to the danger of drying them in the water oven at 100°. M. O. F.

**Decomposition Products of Glucose.** By ALLEIN and F. GAUD (*J. Pharm.*, 1894, [5], **30**, 300—305).—In the estimation of glucose by Fehling solution, it is known that a part of the glucose present escapes estimation. Gaud finds that this loss may be expressed by the formula  $y = -0.00004801x + 0.02876359x^2$ , where  $x$  = the true titre of the sugar solution and  $y$  = the error. With a view to discover the source of this error, the authors have investigated the liquors resulting from a large number of estimations. Besides tartaric acid (which they consider as the main product of the action), the authors obtain lactic, dihydroxyphenylpropionic, melassic, and glucic acids and catechol. They, therefore, believe that the error of

the Fehling reaction is due to the decomposing action of the alkali on a part of the glucose before the latter has been able to exert its reducing action on the copper solution. They propose substituting an ammoniacal solution of copper sulphate for the Fehling solution (see this vol., ii, 92).

L. T. T.

### **Influence of Certain Proteïds on Solutions of Glycogen.**

By H. SCHWIENING (*Pflüger's Archiv*, 1894, **58**, 222—228).—Sugar often forms in solutions of glycogen mixed with proteïd, and the hypothesis has been advanced that the proteïd is the source of the ferment. In the present research, various forms of proteïd were added to solutions of glycogen, but the results were most irregular, and do not settle the question, as sugar sometimes appeared in the sterilised, sometimes in the unsterilised, samples.

W. D. H.

**Fungus Cellulose.** By E. WINTERSTEIN (*Zeit. physiol. Chem.*, 1894, **20**, 342; compare Abstr., 1894, ii, 425).—E. Gilson (*La Cellule*, **11**, 1894) has described a nitrogenous substance mycosine,  $C_{14}H_{28}N_2O_{10}$ , which he has separated from the cell membrane of fungi.

The present communication urges a claim for priority, the author being the first to point out the presence of nitrogen compounds mixed with the cellulose of fungi. From the results of his analyses, he doubts whether it is a single substance.

W. D. H.

### **Nitrogenous Decomposition Product of Fungus Cellulose.**

**A Correction.** By E. WINTERSTEIN (*Ber.*, 1894, **27**, 3508—3509).—In his previous paper on this subject (this vol., i, 80), it was stated that *Boletus edulis*, *Agaricus campestris*, and *Morchella esculenta*, when fused with potassium hydroxide at  $180^\circ$ , yield nitrogenous fungus cellulose; the substance cannot, however, be unaltered cellulose, as it is soluble in highly dilute hydrochloric acid (compare Abstr., 1894, ii, 425).

J. B. T.

**Isonitramines.** By W. TRAUBE (*Ber.*, 1894, **27**, 3291—3293; compare Abstr., 1894, i, 400).—Sodiummethylenedi-isonitramine has been obtained by MacDonald and Masson (*Trans.*, 1894, 944) by the action of nitric oxide on an alcoholic solution of sodium ethoxide, whilst the author has always prepared it by adding acetone to this mixture. The constitution of the isonitramine group is probably

represented by the formula  $O < \begin{smallmatrix} \text{NR} \\ | \\ \text{N} \cdot \text{OH} \end{smallmatrix}$  or  $\text{RN}:\text{NOH}$  (*sic*; ?  $\text{RN}:\text{NO} \cdot \text{OH}$ ),

since methylenedi-isonitramine, when reduced by sodium amalgam, yields hydrazine and ammonia, whilst with acid reducing agents it is converted into methylamine. The formula proposed by MacDonald and Masson,  $\text{CH}_2[\text{N}(\text{NO}) \cdot \text{OH}]_2$  is rendered improbable by the fact that the nitrosohydroxylamine derivatives described by Wohl (Abstr., 1894, i, 409) and Bamberger (Abstr., 1894, i, 412) have properties which differ entirely from those of the isonitramines. When the salts of methylenedi-isonitramine are heated with hydrochloric acid, nitrous oxide and nitrous acid are evolved, whilst formaldehyde and hydroxylamine are also formed, together with a little hydrocyanic acid. It is prob-

able that formoxime is first produced, and this is confirmed by the fact that when the di-isonitramine of benzylic cyanide is treated in the same way, the isonitroso-compound can be isolated. The isonitramines corresponding with diethyl ketone, dipropyl ketone, deoxybenzoin, the substituted ethylic acetoacetates, ethylic malonate, and its substituted derivatives, phenylacetic acid, the nitroparaffins, and the 1:3-diketones have all been prepared and are being further examined. A. H.

### Hydroxylamineacetic and $\alpha$ -Hydroxylaminepropionic acids.

By A. WERNER and E. SONNENFELD (*Ber.*, 1894, **27**, 3350—3354).—Hydroxylamineacetic acid is a syrup, which dries to a gummy mass.

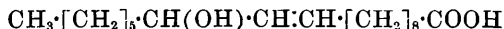
$\alpha$ -Hydroxylaminepropionic acid was prepared in the same way as hydroxylamineacetic acid (Abstr., 1893, i, 501), using ethylic  $\alpha$ -bromopropionate instead of chloracetate.  $\alpha$ -Benzenylamidoximepropionic acid hydrochloride,  $\text{NH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{O}\cdot\text{CHMe}\cdot\text{COOH}\cdot\text{HCl} + \text{H}_2\text{O}$ , melts at  $168^\circ$ ; the acid itself melts at  $129^\circ$ , and its *esoanhydride* at the same temperature. The acid, when diazotised in hydrochloric acid solution, yields  $\alpha$ -benzenylchloroximepropionic acid,



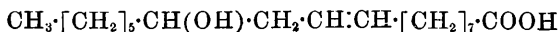
which melts at  $102^\circ$ . This, when treated with sodium ethoxide, yields  $\alpha$ -ethylbenzhydroximepropionic acid, which forms a *hydrochloride* decomposing at  $168^\circ$ , and, when heated with strong hydrochloric acid, yields  $\alpha$ -hydroxylaminepropionic acid,  $\text{NH}_2\cdot\text{O}\cdot\text{CHMe}\cdot\text{COOH}$ , which was obtained as a soft, gummy mass. C. F. B.

**Decomposition of Fatty Acids by Oxidation at Ordinary Temperatures in the absence of Ferments.** By O. FRANK (*Chem. Centr.*, 1894, i, 1143; from *Arch. Physiol.*, 1894, 51—57).—The salts of the higher fatty acids, such as oleic and stearic acids, are decomposed by the oxygen of the air at ordinary temperatures, especially when the oxidised acid, which is formed, is removed from the sphere of action. This decomposition is especially important in the case of ethereal extracts of animal tissues, such as occur in the separation of cholesterol from fat by Hoppe-Seyler's method, where the fat is hydrolysed and extracted with ether. This method gives results which are too high. By employing basic salts, the oxidation of the fatty acid can be considerably lessened. E. C. R.

**Constitution of Ricinoleic acid and its Derivatives.** By P. WALDEN (*Ber.*, 1894, **27**, 3471—3478).—According to the formulæ proposed for ricinoleic acid by Krafft,



(Abstr., 1888, 1270), and Goldsobel,



(this vol., i, 81), this substance contains an asymmetric carbon atom as well as an ethylenic linking. The author has studied the application of the stereochemical theory to this compound and its deriva-

tives, and has also determined their behaviour towards polarised light. Three isomeric acids,  $\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{COOH}$ , are known. Ricinoleic acid, melting at  $16-17^\circ$ , is optically active and dextrorotatory,  $[\alpha]_D = 6.25^\circ$  to  $7.5^\circ$ . Ricinelaïdic acid, melting at  $53^\circ$ , is also dextrorotatory; in acetone solution at  $20^\circ$ ,  $[\alpha]_D = 4.8^\circ$  to  $5.4^\circ$ . Ricinic acid, melting at  $81-82^\circ$ , is optically inactive. A fourth isomeric acid was obtained on one occasion by heating barium ricinelaïdate in a vacuum. It melts at  $75^\circ$ , and is optically inactive.

Two isomeric fatty acids,  $\text{C}_{17}\text{H}_{31}\cdot\text{COOH}$ , have been obtained by heating the two optically active, unsaturated acids or their barium salts. That prepared from ricinoleic acid melts at  $44-45^\circ$ , whilst the isomeride melts at  $53-54^\circ$ ; both are optically inactive.

Two isomeric trihydroxy-acids are formed by the oxidation of ricinoleic acid with potassium permanganate. One of these melts at  $110-111^\circ$ , and is levorotatory. In acetic acid solution,  $[\alpha]_D = -6.25^\circ$  to  $-6.0^\circ$ . The other melts at  $140-142^\circ$ , and is probably optically active, although the author has not examined it. The corresponding acid, obtained from ricinelaïdic acid, melts at  $114-115^\circ$ , and is also probably optically active.

These facts are all consistent with the supposition that ricinoleic acid is related to ricinelaïdic acid in the same way as maleic to fumaric acid.

A number of other compounds were also examined with respect to their optical activity. Castor oil itself is dextrorotatory,  $\alpha_D =$  about  $+3^\circ$  for a length of 100 mm. Ceanthol, undecylenic acid, and caprylic acid, prepared from ricinoleic acid, are optically inactive. The *phenylhydrazide* of *ricinoleic acid*, melting at  $62-63^\circ$ , is dextrorotatory,  $[\alpha]_D = +6.6^\circ$  in alcoholic solution. The corresponding derivative of ricinelaïdic acid melting at about  $110^\circ$  is also dextrorotatory,  $[\alpha]_D = +7.0^\circ$  in alcoholic solution, whilst that of ricinic acid, which melts at  $110-110.5^\circ$ , is inactive. Ricinostearolic acid,  $\text{OH}\cdot\text{C}_{17}\text{H}_{30}\cdot\text{COOH}$ , prepared from ricinoleic acid, is dextrorotatory,  $[\alpha]_D = +13.67^\circ$  in solution in acetone. Sulphoricinic acid is inactive.

A. H.

**Fusion of Stearolic and Behenolic acid with Potash.** By M. BODENSTEIN (*Ber.*, 1894, **27**, 3397—3405).—Marasse (*Ber.*, **2**, 359) obtained hypogæic and myristic acids on fusing stearolic acid with caustic potash, 1 mol. of acetic acid being eliminated at each stage of the decomposition. The author has confirmed this observation, and determined the constitution of the former acid in the following manner (compare J. Baruch, *Abstr.*, 1894, i, 170).

Palmitolic acid,  $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{C}:\text{C}:[\text{CH}_2]_5\cdot\text{COOH}$ , is obtained from hypogæic acid by hydrolysis of the dibromide with alcoholic potash. When treated with concentrated sulphuric acid, it yields ketopalmitic acid,  $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CO}:[\text{CH}_2]_5\cdot\text{COOH}$ , which is converted by hydroxylamine into ketoximepalmitic acid,  $\text{C}_8\text{H}_{17}\cdot\text{C}(\text{NOH})\cdot[\text{CH}_2]_5\cdot\text{COOH}$ . Warm concentrated sulphuric acid effects molecular rearrangement of this substance, and the product, when heated with fuming hydrochloric acid at  $180-200^\circ$ , yields octylamine and pelargonic, amidoheptylic, and suberic acids. Hypogæic acid is, therefore, represented by the formula  $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}:\text{CH}:[\text{CH}_2]_5\cdot\text{COOH}$ .

*Ketopalmitic acid* melts at  $74^{\circ}$ . The acid, formed on warming ketoximepalmitic acid with concentrated sulphuric acid, crystallises from glacial acetic acid, and melts at  $57.5-58^{\circ}$ .

*Icosenic acid*,  $C_{20}H_{38}O_2$ , is formed when behenolic acid is heated with fused caustic potash at  $250-270^{\circ}$ ; it melts at  $50^{\circ}$ , and boils at  $267^{\circ}$  under a pressure of 15 mm. The sodium and barium salts crystallise from alcohol; the silver salt is blackened by light, and the lead salt crystallises from ether. The dibromide, when hydrolysed with alcoholic potash, yields *icosinic acid*,  $C_{20}H_{36}O_2$ , which melts at  $69^{\circ}$ , and boils at  $270^{\circ}$  (15 mm.). Stearic acid is the sole product of the action of fused potash on behenolic acid when the temperature is maintained at  $280-300^{\circ}$ .

Attention is drawn to the points of analogy existing among members of the oleic acid series. M. O. F.

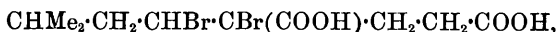
**Ethylic Formylsuccinate.** By W. WISLICENUS (*Ber.*, 1894, 27, 3186—3189).—This substance is obtained by the action of dry sodium ethoxide suspended in ether on a mixture of ethylic succinate and formate; its copper derivative melts at  $134-136^{\circ}$ . Anderlini and Bovisi (*Abstr.*, 1893, i, 193), for unknown reasons, assign the formula  $COOEt \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOEt$  to this product. It should, of course, be  $COOEt \cdot CH_2 \cdot CH(CHO) \cdot COOEt$ ; or, perhaps more probably,  $COOEt \cdot CH_2 \cdot C(CH_2OH) \cdot COOEt$ , in which case it is the ethylic salt of the acid of which Fittig's aconic acid (*Abstr.*, 1883, 458) is the lactone. It yields a sodium derivative, reacts with phenylhydrazine, can be reduced to ethylic itamalate (which boils at  $110^{\circ}$  under 15 mm. pressure), and is readily hydrolysed to alcohol and formic and succinic acids. C. F. B.

**Condensation of Aldehydes with Glutaric acid.** By R. FITTIG (*Annalen*, 1894, 282, 334—338).—General and introductory remarks on the papers of Roedel (this vol., i, 141) and Bronnert (next abstract). A. R. L.

**Condensation of Isovaleraldehyde with Glutaric acid.** By R. FITTIG and E. BRONNERT (*Annalen*, 1894, 282, 344—362).—*Isovalerylideneglutaric acid*,  $CHMe_2 \cdot CH_2 \cdot CH : C(COOH) \cdot CH_2 \cdot CH_2 \cdot COOH$ , is formed by heating a mixture of isovaleraldehyde, sodium glutarate, and acetic anhydride at  $150^{\circ}$ ; it is also produced by the interaction of isovaleraldehyde with ethylic glutarate and sodium ethoxide (Claisen's reaction, *Abstr.*, 1890, 891). The latter method is the more convenient, as the product is more easily purified; from ethylic glutarate (100 grams), isovalerylglutaric acid (3 grams), and diisovalerylglutaric acid (10 grams) are obtained. If metallic sodium is used instead of sodium ethoxide, there are obtained from ethylic glutarate (28 grams), isovalerylideneglutaric acid (1 gram), and diisovalerylideneglutaric acid (4 grams). Isovalerylideneglutaric acid crystallises from water in small plates, and melts at  $75^{\circ}$ ; sodium amalgam is without action on the acid, but reduction appears to take place with hydriodic acid and phosphorus at  $170^{\circ}$ . The barium and calcium salts crystallise with 1 mol.  $H_2O$ , and are less soluble in hot than cold

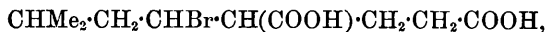
water; the *silver* salt is a white precipitate, stable towards light and insoluble in water.

*Dibromisoamyloglutaric acid*,



is prepared by treating a solution of isovalerylideneglutaric acid in carbon bisulphide with bromine in diffused sunlight; it melts at 148°.

*Bromisoamyloglutaric acid*,



is prepared by treating isovalerylideneglutaric acid with a saturated solution of hydrogen bromide in glacial acetic acid at 0°; it melts at 109°. The constitution of the acid is proved by the fact that when boiled with water for eight hours it yields an acid isomeric with the above-described isovalerylideneglutaric acid; this melts at 117·5°, and

is probably the *lactonic acid*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CH}(\text{COOH}) \\ \text{O} - \text{CO} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ ,

The chief product of the interaction of the brominated acid with water is, however, *isononenic acid* (*isovalerylidenebutyrac acid*),  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which is a colourless liquid volatile with steam. The *calcium* salt crystallises with 9H<sub>2</sub>O, and the *barium* salt with 1½H<sub>2</sub>O, whilst the *silver* salt is a white, amorphous precipitate which becomes brown when heated with water. *Dibromisononylic acid*, C<sub>9</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub>, obtained by brominating isononenic acid in diffused sunlight, forms asymmetric crystals, *a* : *b* : *c* = 0·6829 : 1 : 0·32876, and melts at 66°. When isovalerylideneglutaric acid is distilled, an oil, consisting of the *anhydride*, C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>, passes over at 320°.

*Diisovalerylideneglutaric acid*, CH<sub>2</sub>[C(COOH):CH·CH<sub>2</sub>Pr<sup>s</sup>]<sub>2</sub> (mentioned above), can be prepared from its calcium salt, which is almost insoluble in water; it crystallises from acetone in lustrous, monosymmetric tablets, *a* : *b* : *c* = 4·8644 : 1 : 2·2147, melts at 220°, commences to decompose at 240°, and is as good as insoluble in cold water. The *silver* salt is a white precipitate soluble in hot water, and in the dry state is stable towards light. *Diisovalerylideneglutaric acid* forms a *dibromide*, C<sub>15</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>4</sub>, which melts and decomposes at 185—186°, and yields the original non-brominated acid when treated with sodium amalgam; it also forms a *tetrabromide*, C<sub>15</sub>H<sub>24</sub>Br<sub>4</sub>O<sub>4</sub>, melting at 172°, and a *dihydrobromide*, C<sub>15</sub>H<sub>26</sub>Br<sub>2</sub>O<sub>4</sub>, melting at 174°, and decomposing at 180°.

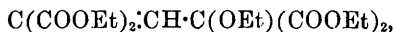
A. R. L.

**Aconic acid.** By H. REITTER (*Ber.*, 1894, **27**, 3440—3441).—Methylic aconate is best prepared by simply dissolving the acid in methylic alcohol at a gentle heat and allowing the solution to remain.

It reacts with phenylhydrazine to form a compound, C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>, which crystallises in white needles and melts at 167°. It is possibly a hydrazone-hydrazide of methylic formylsuccinate (compare Wislicenus, this vol., i, 127). Aconic acid also reacts with phenylhydrazine, forming a substance which is probably the hydrazone-dihydrazide of methylic formylsuccinate. It crystallises in colourless needles and melts at 178—179°.

A. H.

**Ethylic Allylenetetra-carboxylate.** By N. ZELINSKY and A. DOROSCHESKY (*Ber.*, 1894, **27**, 3374—3376).—When an alcoholic solution of ethylic disodiummalonate is boiled with carbon tetrachloride, a reaction takes place with separation of sodium chloride. After distilling off the alcohol and unaltered carbon tetrachloride, water is carefully added, the product of the reaction then separating as a yellow, granular crystalline mass, which is purified by recrystallisation from alcohol. The authors expected that this would prove to be *ethylic allylenetetra-carboxylate*,  $C(COOEt)_2 \cdot C:C(COOEt)_2$ , but it was found that the substance still contains considerable quantities of sodium; on analysis it was found to have the composition  $C_{17}H_{25}O_9Na$ , and is, therefore, an additive compound of ethylic allylenetetra-carboxylate and sodium ethoxide, the constitution of which is probably represented by the formula  $CNa(COOEt)_2 \cdot C(OEt)(COOEt)_2$ . On treatment with sulphuric acid, it is converted into the corresponding *ethylic ethoxypropylenetetra-carboxylate*,



which separates as a colourless oil; on attempting to distil it under 30 mm. pressure, alcohol was evolved at a low temperature, and the residual product then passed over at about 200°, solidifying in the receiver to a crystalline mass. The latter, after recrystallisation from boiling ether, forms acicular crystals melting at 93—95°, which, from the method of preparation, must in all probability consist of ethylic allylenetetra-carboxylate, a supposition which is confirmed by the analysis. When allowed to remain in a moist atmosphere, it deliquesces, forming a colourless, syrupy liquid having the composition  $C_{15}H_{20}O_8 + 2H_2O$ . Further experiments with this substance are in progress, and attempts are being made to obtain free allylenedicarboxylic acid.

H. G. C.

**Uroxanic and Oxonic acids.** By E. SUNDWIK (*Zeit. physiol. Chem.*, 1894, **20**, 335—341).—An alkaline solution of uric acid, when kept for some months in a closed vessel, deposits crystals of the uroxanate and oxonate of the alkali. These simple oxidation derivatives of uric acid (uroxanic acid,  $C_4H_5N_3O_4$ , and oxonic acid,  $C_5H_5N_4O_6$ ) can, however, be prepared more rapidly as follows. If potassium permanganate is added to uric acid suspended in water, allantoin is formed; but if the permanganate is added very carefully and gradually in the cold to an alkaline solution, uroxanic acid is obtained, which crystallises out after the manganese dioxide has been filtered off. Its silver, sodium, potassium, barium, and calcium salts were prepared.

Oxonic acid is prepared from the mother liquor from which the uroxanate has crystallised, by boiling, filtering, and then adding acetic acid in the cold.

W. D. H.

**Nature of the Aluminium Chloride Reaction.** By C. RADZIEWANOWSKI (*Ber.*, 1894, **27**, 3235—3238).—In the synthesis of aromatic hydrocarbons by the action of alkylic haloïds on benzene and analogous compounds, a large amount of the material is lost, owing to the formation of higher alkylated compounds. The yield of a

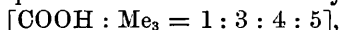
hydrocarbon, such as ethylbenzene, may be greatly increased by using a larger amount of the solvent, in this case benzene, and, still further, by treating the higher boiling products with benzene and aluminium chloride, when these are converted into ethylbenzene. The yield of diphenylmethane from benzylic chloride and benzene may be increased in a similar manner, although not to so great an extent; the best results are obtained by using a large excess of benzene and keeping the mixture at 7°. In addition to diphenylmethane, two hydrocarbons are formed, melting at 86° and 78° respectively, and identical with the  $\alpha$ - and  $\beta$ -dibenzylbenzenes described by Zincke (this Journal, 1873, 631; 1876, i, 703) and Baeyer (this Journal, 1873, 884); the best yield of these hydrocarbons is obtained by the action of 30 grams of benzylic chloride on 150 grams of diphenylmethane in presence of 7 grams of aluminium chloride.

When benzylic chloride (2 mols.) and benzene (1 mol.) are treated with aluminium chloride in carbon bisulphide solution, the chief product is the insoluble substance obtained by Perkin and Hodgkinson (Trans., 1880, 726), by the direct treatment of benzylic chloride with aluminium chloride. Friedel and Crafts regard this substance as a polymeric diphenylene,  $(C_6H_4:CH_2)_x$ , and this is in agreement with the fact that it is converted, by an excess of benzene and aluminium chloride, into diphenylmethane.

When diphenylmethane and asymmetrical diphenylethane are acted on by aluminium chloride in absence of benzene, they yield anthracene and mesodihydrodimethylantracene respectively; as these hydrocarbons are also formed by the action of aluminium chloride on benzylic chloride and  $\alpha$ -chloroethylbenzene respectively, it is evident that, in the above synthesis, the first action is the elimination of a phenyl group with formation of the chloride of the aromatic hydrocarbon residue, which then undergoes condensation into the corresponding anthracene hydrocarbon with elimination of hydrogen chloride.

H. G. C.

**Derivatives of Isodurene.** By P. JANNASCH and M. WEILER (Ber., 1894, 27, 3441—3448).—Isodurene is converted by bromine water into the dibromo-compound melting at 199°, no other derivative being formed. *Dinitroisodurene*, melting at 181°, is formed by the direct nitration of the hydrocarbon, and is accompanied by a smaller amount of dinitroxylene, melting at 112°. A dinitroisodurene, melting at 156° or 165°, could not be obtained (compare Jacobson, Abstr., 1883, 52; Ador and Rilliet, Abstr., 1879, 527). When the hydrocarbon is heated with dilute nitric acid at 115—130°, three monobasic acids are produced. These are isodurylic acid



mesitylenecarboxylic acid  $[COOH : Me_3 = 1 : 2 : 4 : 6]$ , and  $\beta$ -isodurylic acid  $[COOH : Me_3 = 1 : 2 : 3 : 5]$ . The last-named acid has not been previously obtained pure; it crystallises in needles, and yields a calcium salt, which crystallises well. The acid may readily be separated from mesitylenecarboxylic acid by etherification, as the latter is not altered by treatment with alcohol and hydrogen chloride.

A. H.

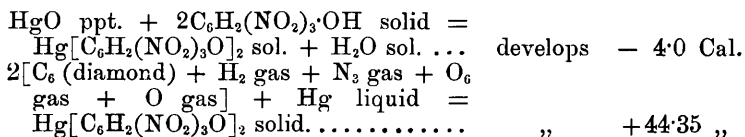


*Paradicesylic thiocarbonate*,  $\text{CS}(\text{O}\cdot\text{C}_7\text{H}_7)_2$ , crystallises from alcohol in white needles, which melt at  $132^\circ$ . *Dithymylic thiocarbonate*,  $\text{CS}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_2$ , forms white plates, and melts at  $110^\circ$ .  *$\beta$ -Dinaphthyllic thiocarbonate*,  $\text{CS}(\text{O}\cdot\text{C}_{10}\text{H}_7)_2$ , crystallises from benzene in snowy plates, which melt at  $212^\circ$ ; the *dibromo-derivative*,  $\text{C}_{21}\text{H}_{12}\text{Br}_2\text{O}_2\text{S}$ , crystallises from glacial acetic acid in minute plates, which melt at  $171^\circ$ .  *$\beta$ -Dinaphthyllic thiocarbonate* is analogous to diphenylic thiocarbonate in its behaviour towards ammonia and amines (*loc. cit.*). M. O. F.

H. G. C.

The action of acids on mercuric picrate, and of other mercuric salts on picric acid and alkali picrates, yield the following numbers.

Heat of dissolution of anhydrous mercuric picrate ..	- 4·7 Cal.
" " hydrated " "	- 12·4 "
Heat of hydration of mercuric picrate (liquid H <sub>2</sub> O)	+ 7·7 "
HgO ppt. + 2C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> OH diss. =	
Hg[C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> O] <sub>2</sub> diss. + H <sub>2</sub> O, liquid develops	+ 6·2 "



In the value of the heat of neutralisation, mercuric picrate resembles the acetate. It is noteworthy that, whereas picric acid will completely displace hydrocyanic acid from dissolved potassium cyanide, with development of +10·7 Cal., hydrocyanic acid completely displaces picric acid from dissolved mercuric picrate, with development of +12·2 Cal.

C. H. B.

### Action of Picric Acid and Picrates on Metallic Cyanides.

By R. VARET (*Compt. rend.*, 119, 562).—Isopurpurates are not formed by the action of mercuric cyanide on picric acid or picrates, and the author has shown (preceding abstract) that hydrocyanic acid completely displaces picric acid from mercuric picrate. This result affords further proof of the author's general conclusion (*Abstr.*, 1891, 681) that, in the action of picric acid and picrates on metallic cyanides, isopurpurates are always formed if the picric acid displaces hydrocyanic acid from the particular cyanide, but are not formed if hydrocyanic acid displaces the picric acid, the inverse displacements being determined by the thermochemical disturbances.

C. H. B.

**The Bleaching Powder Reaction for Aniline.** By R. NIETZKI (*Ber.*, 1894, 27, 3263—3264).—The well known bleaching powder reaction for aniline can be readily obtained by adding an excess of the reagent to a solution of aniline in water, and is given in equal intensity by commercial aniline and by aniline prepared with the greatest care from pure materials. The reaction must, therefore, be considered as due to the aniline itself and not to any impurity. (Compare Hantzsch and Freese, *Abstr.*, 1894, i, 572; this vol., i, 24).

A. H.

**Thioaniline.** By R. NIETZKI and H. BOTHOF (*Ber.*, 1894, 27, 3261—3263).—*Paradinitrophenylic sulphide* is formed when paranitrochlorobenzene, in alcoholic solution, is heated with sodium sulphide; it crystallises in yellow plates, melting at 154°. When reduced with zinc dust and acetic acid, it is converted into the thioaniline described by Merz and Weith; this result does not agree with that arrived at by K. A. Hofmann (this vol., i, 87), who looks on this substance as an ortho-compound.

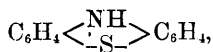
A. H.

**New Modes of Formation of Thiodiphenylamine.** By K. A. HOFMANN (*Ber.*, 1894, 27, 3320—3324; compare this vol., i, 87).—When aniline is heated with sulphur and hydrochloric acid at 170—200°, it seems that paradiamidophenylic bisulphide,



is first formed, and that this then condenses with aniline to form

monophenyldiamidophenylic bisulphide,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , which then breaks up partly into thiodiphenylamine,



and paramidothiophenol,  $\text{SH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . The actual products of the action are thiodiphenylamine and *phenyldiamidophenylic bisulphide*. The latter crystallises in yellow needles, and oxidises readily in the air; when reduced with tin and hydrochloric acid, it decomposes into paramidothiophenol and a basic compound, ( $? \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ ), the hydrochloride of which forms a white, crystalline, readily oxidisable powder.

It will be noticed that in the above formation of thiodiphenylamine a migration of the sulphur atom has taken place from the para- to the ortho- position; other examples of this are cited.

C. F. B.

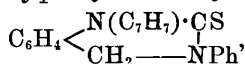
**Benzylorthamidobenzylaniline.** By M. BUSCH and H. ROEGGLEN (*Ber.*, 1894, **27**, 3239—3247).—Hitherto only those derivatives of orthamidobenzylaniline have been prepared, in which substitution has taken place in the aliphatic amido-group. The authors endeavoured to obtain bisubstitution products by the action of alkylic haloids on the monosubstituted derivatives, but without success. The unsymmetrical dibenzyl-derivative may, however, be prepared indirectly by acting on orthamidobenzylaniline with benzaldehyde, and reducing the resulting benzylidineorthamidobenzylaniline,



with sodium in alcoholic solution. The latter compound crystallises in spear-shaped needles melting at  $107\text{--}108^\circ$ , and is resolved by dilute sulphuric acid into its constituents. The product of reduction, *benzylorthamidobenzylaniline*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}$ , crystallises from alcohol in spherical aggregates of lustrous, colourless plates, melting at  $88^\circ$ ; it is a weak di-acid base, the *dihydrochloride*,  $\text{C}_{20}\text{H}_{20}\text{N}_2\cdot 2\text{HCl}$ , crystallising in colourless needles which decompose and melt at about  $170^\circ$ , and are dissociated by water. With acetic anhydride, both hydrogen atoms of the imido-groups are displaced by acetyl groups with formation of *diacetylbenzylorthamidobenzylaniline*,  $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPhAc}$ , which crystallises in slender, colourless needles melting at  $173^\circ$ ; it behaves, therefore, towards this reagent in a manner different from the corresponding symmetrically substituted orthodiamine, which only takes up one acetyl group with formation of a ring derivative.

Nitrous acid acts on benzylorthamidobenzylaniline with formation of the *dinitroso*-derivative,  $\text{C}_{20}\text{H}_{18}\text{N}_2(\text{NO})_2$ , which crystallises in fascicular aggregates of colourless plates melting at  $124^\circ$ ; on reduction with zinc dust and acetic acid, it yields the monhydrazine derivative, the second nitroso-group being eliminated as ammonia. The *hydrazine* derivative,  $\text{C}_{20}\text{H}_{21}\text{N}_3$ , crystallises in tufts of white needles melting at  $110^\circ$ , and with benzaldehyde yields a *hydrazone*, crystallising in pale yellow needles melting at  $140\text{--}142^\circ$ .

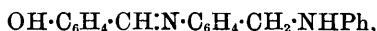
When benzylorthamidobenzylaniline is heated on the water bath with benzaldehyde, it is converted into *benzylldiphenyltetrahydroquinazoline*,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}(\text{C}_7\text{H}_7) \cdot \text{CHPh} \\ \text{CH}_2 - \text{NPh} \end{smallmatrix}$ , which crystallises in colourless needles melting at  $120^\circ$ ; the tetrahydroquinazoline ring is opened very readily, dilute sulphuric acid converting the above compound into its constituents on gentle heating. The corresponding 1' : 2' : 3'-*benzylhydroxyphenyltetrahydroquinazoline* is prepared in a similar way from salicylaldehyde and the diamine, and forms clear, colourless prisms melting at  $172^\circ$ . Carbon bisulphide does not act on the diamine at all readily, but at  $180^\circ$  an action takes place; the compound formed, however, is the same as the phenylthiotetrahydroquinazoline obtained from orthamidobenzylaniline, one of the benzyl groups being eliminated in the reaction. The *benzylphenylthiotetrahydroquinazoline*,



may, however, be obtained by heating the former compound with benzylic chloride, and crystallises in colourless needles melting at  $93^\circ$ . The entrance of the benzyl group into the molecule gives to the compound basic properties; the *nitrate*,  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{S} \cdot \text{HNO}_3$ , crystallises in large, transparent needles melting at  $126^\circ$  with evolution of gas.

Carbonyl chloride acts on benzylorthamidobenzylaniline, but does not form a ring derivative, the substance obtained having probably the constitution  $\text{CH}_2\text{Ph} \cdot \text{N}(\text{COCl}) \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{COCl}$ ; it crystallises in transparent prisms melting at  $113^\circ$ .

The following compounds have also been obtained by the action of salicylaldehyde and orthonitrobenzaldehyde on orthamidobenzylaniline; *orthohydroxybenzylidineorthamidobenzylaniline*,



crystallising in yellow needles and melting at  $124^\circ$ , and *ortho-nitrobenzylidineorthamidobenzylaniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NPh}$ , crystallising in yellow plates and melting at  $132-134^\circ$ .

H. G. C.

**Paranitrodiazobenzene Methyl Ether.** By E. BAMBERGER (*Ber.*, 1894, **27**, 3412—3420).—A detailed criticism of the arguments put forward by Hantzsch (this vol., i, 26) supporting his view that the ether is an "anti-" derivative. The author still regards it as a normal diazo-compound, and although this cannot be directly shown by hydrolysis, the hydrolytic conversion of diazobenzene methyl ether and parabromodiazobenzene methyl ether into the corresponding normal diazo-salts lends support to the view. M. O. F.

**Action of Phthalic Chloride on Dinitrodiazoamidobenzenes.** By B. PAWLEWSKI (*Ber.*, 1894, **27**, 3430—3431).—*Paranitrophthalanil*,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is formed when paradinitrodiazoamidobenzene is heated with phthalic chloride. It is a colourless, insoluble powder, which melts at  $262-264^\circ$ .

Metanitrophthalanil is obtained in a similar manner from metadi-nitrodiazoamidobenzene; the same product is formed on fusing a mixture of metanitriline and phthalic anhydride (Gabriel, *Ber.*, **11**, 2260). It crystallises from boiling glacial acetic acid in long needles which melt at 242—244°.

The action of phthalic chloride on nitranilines gives rise to nitro-phthalanil-derivatives. M. O. F.

**Alkylated Azo-compounds, and the Theory of Dyeing.** By R. MEYER and J. SCHÄFER (*Ber.*, 1894, **27**, 3355—3361).—In the dyeing of fabrics of animal origin, it is generally supposed that a union takes place between the fabric and the colouring matter, as only colouring-matters containing a salt-forming group, such as the hydroxy- or amido-group, are capable of direct dyeing. In the case of vegetable fabrics, which consist almost entirely of cellulose, it is difficult to suppose that any such combination takes place, as the cellulose shows so little tendency to enter into chemical combination; at the same time, it is remarkable that, as a rule, only those colouring matters containing salt-forming groups do dye vegetable fabrics directly. Certain cases are, however, known in which compounds supposed to contain no such group dye cotton directly, and the authors have examined some of these cases more closely.

The first colouring matter examined was that known as chryso-phenin, which is obtained by the ethylation of "Brilliantgelb," and is usually supposed to have the constitution



The analysis of its salts has, however, shown that instead of two ethoxyl groups it contains one ethoxyl group and one hydroxyl group, and this is confirmed by the fact that, on treatment with zinc dust and acetic acid, it yields both paramidophenetoil and paramidophenol. Another colouring matter which is supposed to contain no salt-forming group, although it dyes cotton directly, is obtained from diamidonaphthalenedisulphonic acid, and to it is assigned the constitution  $\text{C}_{10}\text{H}_4(\text{SO}_3\text{Na})_2(\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ ; further investigation, however, has shown that in this case also only one of the hydroxyl groups is ethylated.

Attempts were then made by the authors to obtain the dibenzyl derivative of "Brilliantgelb,"  $\text{C}_2\text{H}_2[\text{C}_6\text{H}_3(\text{SO}_3\text{Na})\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_7\text{H}_7]_2$ , but it was found impossible to displace the hydrogen atoms of both hydroxyl groups, only the monobenzyl derivative being obtained. An endeavour was next made to obtain the dialkyl derivative of a bisazo-compound containing no sulphonic groups, diphenylbisazophenol being selected, and subjected to the action of benzylic chloride and soda. Here again, however, the action stopped with the formation of the monobenzyl derivative. In all the cases examined, therefore, the alkyl derivatives of symmetrical hydroxyazo-compounds have proved to be unsymmetrical mono-ethers. H. G. C.

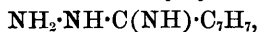
**Action of Alkalis on Orthonitrophenylhydrazine.** By R. NIETZKI and E. BRAUNSCHWEIG (*Ber.*, 1894, **27**, 3381—3384).—The preparation of azoimide by the action of alkalis on dinitrobenzene-

diazoimide led one of the authors to try whether it was not possible to obtain hydrazine in a similar manner by the action of alkalis on orthonitrophenylhydrazinesulphonic acid; it was found, however, that hydrazine is not formed in this manner, but, on the addition of acids, a colourless, crystalline compound separated. As this appeared to belong to a new class of compounds, the authors have studied the action more closely, using, however, the simpler orthonitrophenylhydrazine. The latter is very readily acted on by warm alkalis, even by aqueous ammonia, and, on the addition of acids, the product of the reaction separates in colourless needles melting at  $157^{\circ}$ , and having the composition  $C_6H_5N_3O$ ; it is therefore formed from orthonitrophenylhydrazine by the removal of the elements of water. It is a fairly strong acid, and yields sparingly soluble salts with the alkaline earth and heavy metals, the *lead* salt forming colourless plates, which explode at  $270^{\circ}$ . It is a very stable substance, and is not acted on by acetic anhydride or reducing agents, and therefore no longer contains a nitro-group. When the lead salt is heated with ethylic iodide at  $180^{\circ}$ , iodine is separated and lead iodide formed, and the solution yields dark crystals, which have a metallic lustre, and resemble the periodides of the ammonium bases. To remove the iodine, it was treated with silver chloride, and the resulting chloride, which does not crystallise, converted into the *platinochloride*  $(C_{10}H_{13}N_3)_2, H_2PtCl_6$ ; the new base is therefore formed by the displacement of one atom of oxygen by two ethyl groups. The same derivatives may also be obtained from azimidobenzene by heating it with ethylic iodide and sodium ethoxide at  $150^{\circ}$ ; the product of the action, when treated with iodine, yields the periodide above described, and this, on treatment with silver chloride and chloroplatinic acid, is converted into a platinochloride identical with that already mentioned. The original substance must therefore be closely allied to azimidobenzene, and, taking into consideration its properties and mode of formation, the authors believe that it has undoubtedly the constitution  $C_6H_4 < \begin{smallmatrix} N(OH) \\ \text{---} \end{smallmatrix} N \gg N$ , and propose to term this class of compound *azimidoles*. The compound obtained by the action of ethylic iodide on both azimidoles and azimidobenzene must then have the constitution  $C_6H_4 < \begin{smallmatrix} NEt_2I \\ \text{---} \end{smallmatrix} N \gg N$ .

The substance obtained by the action of alkalis on orthonitrohydrazinesulphonic acid is the corresponding *azimidolesulphonic acid*; its *disodium* salt,  $C_6H_5N_3Na_2SO_4 + H_2O$ , separates in colourless needles, which are converted by the action of dilute acids into the *monosodium salt*  $C_6H_4N_3SO_3Na + H_2O$ , a sparingly soluble substance, crystallising in needles. The free acid has not yet been prepared.

H. G. C.

**Action of Hydrazine on Imidoethers.** By A. PINNER and N. CARO (*Ber.*, 1894, 27, 3273—3291; compare *Abstr.*, 1893, i, 710; 1894, i, 385).—Paratolonylimidoethyl ether reacts in a similar manner to the benzimido-compound. *Paratolonylhydrazidine*,



forms long prisms, which melt and decompose at 75—77°. It is strongly basic, absorbing carbonic anhydride from the air, and has powerful reducing properties. The *carbonate* crystallises in prisms, and melts and decomposes at 100°; the *picrate* melts at 162°, and the *nitrate* at 106° with violent decomposition. In acid solution, it reacts with benzaldehyde to form *benzylidenetolenylhydrazidine*, which crystallises in white plates, and melts at 154°, whilst in alkaline solution, benzaldehyde yields *tolenylhydrazine benzoate*, melting at 244°. *Gly-oxaleneditolenylhydrazidine*,  $C_2H_2[N \cdot NH \cdot C(NH) \cdot C_7H_7]_2$ , forms yellow plates, and melts at 252°. *Paratolyltetrazotic acid*,  $C_7H_7 \cdot C \begin{smallmatrix} N-N \\ || \\ NH \cdot N \end{smallmatrix}$ ,

is obtained by the action of nitrous acid on the hydrazidine; it forms flat prisms, and melts at 234°, becoming red and frothing up at the same time. It is a strong acid, and decomposes carbonates; the *silver salt* is a white, crystalline powder. Acetic anhydride does not yield an acetyl derivative but a mixture of acetyltolylamidine and ditolylmethylcyanidine. It is remarkable that diazobenzene chloride does not give the expected diazo-compound with tolenylhydrazidine, but converts it into tetrazotic acid.

*Benzoyltolenylhydrazidine* crystallises in colourless plates, and melts at 170°. It is soluble both in acids and in alkalis, and acts as a strong reducing agent. When it is heated at 120°, it is converted into the

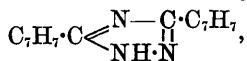
non-reducing *phenyltolyltriazole*,  $C_7H_7 \cdot C \begin{smallmatrix} N-CPh \\ || \\ NH \cdot N \end{smallmatrix}$ , which crystallises in white plates melting at 170°. *Toluoyltolenylhydrazidine* resembles the benzoyl compound, and, when heated, passes into ditolyltriazole, which is described below.

*Ditolenylhydrazidine*,  $N_2[C(C_7H_7) \cdot NH_2]_2$ , forms pale yellow plates, and is sparingly soluble in hot alcohol and acetone. Although stable towards alkalis, it is readily converted by acids into ditolyltriazole, and the same change occurs when it is heated. At 196°, the hydrazidine melts, solidifies again slightly above this temperature, and then finally melts at 248°, the melting point of the triazole. The *hydrochloride* crystallises in stellate groups of needles, the *platinochloride* decomposes above 300°, the *aurochloride* melts at 154—155°, and the *nitrate* at 123°. The *diacetyl* derivative forms long, white needles melting at 185°.

The reaction of ditolenylhydrazidine with nitrous acid is similar to that of dibenzonylhydrazidine. With 2 mols. of sodium nitrite and dilute acetic acid, it yields tolyltetrazotic acid and toluonitrile. With 1 mol. of the nitrite and dilute hydrochloric acid, it forms the hydrochloride of toluoyltolenylhydrazidine, identical with that obtained by the action of toluic chloride on tolenylhydrazidine, whilst with 4 mols. of nitrite and dilute hydrochloric acid, it is converted into the *hydrochloride* of *toluoylnitrosotolenylhydrazidine*,  $C_7H_7 \cdot C(N \cdot NO) \cdot NH \cdot NH \cdot CO \cdot C_7H_7, HCl + \frac{1}{2}H_2O$ . This substance forms colourless prisms, melts and deflagrates at 119°, and, when boiled with water, yields nitrous acid and toluoyltolenylhydrazidine. The free base could not be prepared from the hydrochloride.

*Toluoyltolenylhydrazidine*, the formation of which has been described above, crystallises in short, compact prisms, and is soluble in

strong alkalis and dilute acids. Its *hydrochloride* melts at 203°. Both this salt and the free base reduce copper salts on boiling. When heated, the base is converted into *ditolyltriazole*,



which crystallises from alcohol in colourless prisms, melts at 248°, and sublimes at a higher temperature. It does not reduce copper salts, and is insoluble in dilute acids. The *silver* salt decomposes at 240°. *Acetylditolyltriazole* forms prisms melting at 129–130°.

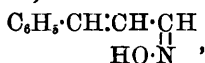
*Ditolyldihydrotetrazine*,  $\text{C}_7\text{H}_7\cdot\text{C}\begin{array}{c} \text{N} \\ \text{NH}\cdot\text{NH} \end{array}\cdot\text{C}\cdot\text{C}_7\text{H}_7$ , crystallises in long, thin, yellow needles, which melt and become red at 235°, ditolyltetrazine (see below) being formed; in the moist state, it oxidises on exposure to air with formation of ditolyltetrazine,  $\text{C}_{16}\text{H}_{14}\text{N}_4$ , and is converted into this substance by other oxidising agents. When boiled with zinc dust and acetic acid, it is reduced, yielding a substance which has the composition of ditolyltriazole; it has not yet been found possible, however, to decide whether it is actually identical or only isomeric with the ditolyltriazole described above. When ditolyldihydrotetrazine is boiled with hydrochloric acid, it is partially converted into the isomeric ditolylisodihydrotetrazine, and partially decomposed with formation of ditolylbiazoxole and hydrazine. *Ditolylisodihydrotetrazine*,  $\text{C}_7\text{H}_7\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{NH} \\ \text{NH}\cdot\text{N} \end{array}\cdot\text{C}\cdot\text{C}_7\text{H}_7$ , crystallises in white prisms, melts without decomposing at 295°, and does not become red when treated with oxidising agents. The *aurochloride* melts at 183°. *Ditolylbiazoxole*,  $\text{C}_7\text{H}_7\cdot\text{C}\begin{array}{c} \text{O}\cdot\text{C}\cdot\text{C}_7\text{H}_7 \\ \text{N}\cdot\text{N} \end{array}$ , which is also formed by the action of sodium nitrite on a hydrochloric acid solution of toluoyltolonylhydrazidine, crystallises in lustrous, flat needles, is insoluble in acids and alkalis, and melts at 233–234°. It unites with 1 mol. of silver nitrate to form a double compound,  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}\cdot\text{AgNO}_3$ , which decomposes above 280°.

*Ditolyltetrazine*,  $\text{C}_7\text{H}_7\cdot\text{C}\begin{array}{c} \text{N}\cdot\text{N} \\ \text{N}\cdot\text{N} \end{array}\cdot\text{C}\cdot\text{C}_7\text{H}_7$ , crystallises in dark bluish-red, flat needles or plates, and melts at 233°. When boiled with alcoholic potash, it yields a compound of the formula,  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$ , the constitution of which has not been determined.

Under certain conditions of experiment, the action of hydrazine on tolenylimido-ether yields *ditolenylimidine*,  $\text{C}_{16}\text{H}_{17}\text{N}_3$ , which crystallises in long, compact needles, and melts at 161°. The *hydrochloride*, melting at 252°, and the *nitrate*, melting at 155°, are only sparingly soluble. The *aurochloride* melts and decomposes at 148°. *Triacetylditolenylimidine* forms colourless needles, and melts at 117°.

A. H.

**anti-Cinnamaldoxime.** By E. BAMBERGER and C. GOLDSCHMIDT (*Ber.*, 1894, 27, 3428–3430).—*anti-Cinnamaldoxime*,





is formed, in addition to the syn-modification, when hydroxylamine hydrochloride is added to cinnamaldehyde suspended in caustic soda. Separation from the isomeride is effected by treatment with light petroleum (b. p. 40—70°); it melts at 64—65°. Hydrogen chloride converts it into the hydrochloride of the syn-oxime. The *acetyl* derivative,  $C_9H_8 \cdot NOAc$ , melts at 35·5°, and during its preparation from the anti-modification the isomeric derivative is also formed; of these two derivatives, the latter only is hydrolysed by warm water.

M. O. F.

**Preparation of Benzoic Anhydride.** By L. CLAISEN (*Ber.*, 1894, **27**, 3182—3184).—Deninger (*J. pr. Chem.*, [2], **50**, 479) has found that benzoic chloride yields benzoic anhydride when treated with anhydrous sodium carbonate; the author has found that the latter, or, equally well, potassium carbonate, will often act as a condensation agent when hydrochloric acid has to be removed. For example, if aniline or phenol is dissolved in ether or benzene, powdered potassium carbonate added, and then benzoic chloride or ethylic chloroformate gradually added, condensation takes place. In a similar manner, it is often possible to replace one or both of the hydrogen atoms in the  $\cdot CO \cdot CH_2 \cdot CO \cdot$  group of 1 : 3-diketones by acid radicles. For example, ethylic acetoacetate yields a mono-benzoic derivative; dibenzoylmethane and benzoylacetone both mono- and di-derivatives.

A convenient modification of the Schotten-Baumann method is also suggested. It is to use alcoholic sodium ethoxide (2 mols.) with 1 mol. of benzoic chloride and 1 mol. of the substance from which a benzoic derivative is to be prepared. The tedious process of shaking is thus avoided.

C. F. B.

**A New Class of Cyclic Iodo-compounds from Iodophenylacetic acid.** By W. RAUM (*Ber.*, 1894, **27**, 3232—3235).—V. Meyer and his co-workers have shown that iodobenzoic acid can be readily converted into iodosobenzoic acid either by oxidation or by conversion into the iodochloride and acting on the latter with water. The iodosobenzoic acid thus formed exists in the two tautomeric forms  $C_6H_4 \cdot \begin{smallmatrix} IO \\ \diagup \\ COOH \end{smallmatrix}$  and  $C_6H_4 \cdot \begin{smallmatrix} I(OH) \\ \diagup \\ CO \end{smallmatrix} \cdot O$ , the latter containing a ring of five atoms. The author has carried out a similar series of reactions with iodophenylacetic acid, in order, if possible, to obtain compounds containing an analogous ring of six atoms.

Orthiodophenylacetic acid was obtained from orthiodotoluene, according to Mabery and Robinson's method, by acting on it with bromine, converting the orthiodobenzylic bromide thus formed into the corresponding nitrile, and subjecting the latter to hydrolysis. The pure acid melts at 110°, and not at 95—96° as stated by Mabery and Robinson. The corresponding *iodochloride*,  $ICl_2 \cdot C_6H_4 \cdot CH_2 \cdot COOH$ , is prepared by passing chlorine into a solution of the acid in chloroform, and forms yellow crystals, which on treatment with water do not yield the iodoso-derivative, but lose hydrogen chloride, forming the compound  $C_6H_4 \cdot \begin{smallmatrix} ICl \cdot O \\ \diagup \\ CH_2 \cdot CO \end{smallmatrix}$ .

From the composition alone, it might be supposed that the new substance was a mixture of the iodochloride with iodophenylacetic acid, but it behaves in all respects as a homogeneous compound, and is insoluble in ether, whereas both the above-named compounds are readily soluble in that liquid. The compound therefore takes an intermediate position between an iodoso-compound and an iodochloride, and contains the nucleus of six atoms whose formation was expected.

Similar experiments with pariodophenylacetic acid have led to totally different results, the iodochloride being reconverted by boiling water or alkalis into the original iodo-acid.

H. G. C.

**Ethyllic Diazoacetate and Picric acid.** By E. BUCHNER (*Ber.*, 1894, 27, 3250—3251).—When ethyllic diazoacetate is treated with picric acid and a little alcohol, nitrogen is evolved, and *ethyllic trinitrophenylglycollate*,  $C_6H_2(NO_2)_3 \cdot O \cdot CH_2 \cdot COOEt$ , remains. It crystallises from alcohol in yellowish needles, and melts at  $102^\circ$ . It is not unlikely that other aliphatic diazo-compounds may react with picric acid in a similar manner, yielding crystalline substances, and this reaction might then be made use of for their recognition.

H. G. C.

**Velocity of Coumarin Formation.** By E. HJELT (*Ber.*, 1894, 27, 3331—3333).—Coumaric, methylcoumaric, and isopropylcoumaric acids exhibit great velocity of coumarin formation, 40, 90, and 70 per cent. respectively undergoing conversion into the anhydride within 40 minutes, and this in spite of the fact that they are  $\delta$ -hydroxy-acids. Probably the double bond conditions the existence of the *cis*-configuration, which is known to be favourable to anhydride formation.

C. F. B.

**Action of Benzylamine on Ethyllic Acetoacetate.** By R. MÖHLAU (*Ber.*, 1894, 27, 3376—3380).—The action of ammonia, methylamine, and diethylamine on ethyllic acetoacetate has been studied by numerous investigators, who have shown that the products are amido-derivatives of ethyllic crotonate. According to the Le Bel-van't Hoff hypothesis, these substances should exist in two stereometric forms, but hitherto no such isomerides have been isolated. The author has therefore examined the action of an amine of higher molecular weight on ethyllic acetoacetate, namely, benzylamine, and has succeeded in obtaining the two stereometric ethyllic benzylamidocrotonates.

When benzylamine (1 mol.) is added to an ethereal solution of ethyllic acetoacetate (1 mol.) at  $-5^\circ$ , an additive product, probably of the constitution  $CH_2Ph \cdot NH \cdot CMe(OH) \cdot CH_2 \cdot COOEt$ , separates in slender needles, but after a time these disappear, and in their place compact crystals are deposited. This compound, which forms about half the product, crystallises in tasteless prisms melting at  $79-80^\circ$ , has the composition and molecular weight of an *ethyllic benzylamidocrotonate*,  $CH_2Ph \cdot NH \cdot CMe \cdot CH \cdot COOEt$ , and is distinguished as the  $\alpha$ -derivative. When heated above its melting point, it is converted into the stereoisomeride, or  $\beta$ -derivative, which is also

contained in quantity in the original product of the action of benzylamine on ethylic acetoacetate, and is formed almost quantitatively if these two substances are not cooled well during the mixing. It crystallises in tabular prisms melting at  $21-21.5^{\circ}$ , is volatile in a current of steam, has a sweet, and at the same time peppery, taste, and, under the influence of light, is gradually transformed into the  $\alpha$ -derivative.

Neither of the isomerides can be distilled, decomposition taking place at  $270-300^{\circ}$ ; methane, hydrogen, and oxides of carbon pass off first, followed by ethylic acetate, acetone, and alcohol, whilst the residue contains dibenzylcarbamide and certain basic compounds.

When benzylamine and ethylic acetoacetate are heated together under pressure, the action proceeds in a different manner, a substance being formed which is either *benzyl- $\beta$ -amidocrotonobenzylamide*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , or *benzyl- $\beta$ -imidobutyrobenzylamide*,  $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , as it is resolved by acids into benzylamine and *benzylacetoacetamide*,



which crystallises in prisms melting at  $96-97^{\circ}$ , and has no basic properties.

That the compounds above described have in reality the constitution assigned to them, and are not the isomeric ethylic benzyl- $\beta$ -imidobutyrate,  $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt}$ , is shown by the fact that benzylamine has no action on ethylic diethylacetoacetate, even at  $100^{\circ}$ .

H. G. C.

**Separation of the Dihydrophthalic Acids.** By W. F. PROOST (*Ber.*, 1894, **27**, 3185).—Dihydrophthalic acid, melting at  $215^{\circ}$  (Astié, *Annalen*, **258**, 188), was prepared, and its acid strychnine salt crystallised. The acid obtained from the crystals gave a sodium salt that was distinctly dextrorotatory; from the mother liquor a levorotatory sodium salt was obtained.

C. F. B.

**Condensation of Benzaldehyde with Glutaric acid.** By R. FITTIG and S. ROEDEL (*Annalen*, 1894, **282**, 338—344).—*Benzylideneglutaric acid*,  $\text{CHPh}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is thus prepared. The product of the interaction of benzaldehyde, sodium glutarate, and acetic anhydride is submitted to distillation in a current of steam, whereby unaltered benzaldehyde is removed; the residue, after preliminary purification, is separated from benzoic and cinnamic acids by conversion into the calcium salts, the salt of the new acid being almost insoluble in hot water. The acid crystallises in silky needles, melts at  $175^{\circ}$ , and is almost insoluble in benzene, chloroform, and carbon bisulphide. The *calcium* and *barium* salts crystallise with  $1\text{H}_2\text{O}$ . The *silver* salt is a white, flocculent precipitate, stable towards light.

*Benzylglutaric acid*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained by reducing benzylideneglutaric acid with sodium amalgam. The *calcium* salt crystallises with  $\frac{1}{2}$  mol.  $\text{H}_2\text{O}$ ; the *barium* salt with

$2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ ; and the *silver* salt is a white precipitate, stable towards light.

*Dibromobenzylglutaric acid*,  $\text{CHPhBr}\cdot\text{CBr}(\text{COOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is prepared by the action of bromine in diffused sunlight on benzylideneglutaric acid suspended in chloroform; it decomposes at  $191-192^\circ$  without melting.

*Bromobenzylglutaric acid*,  $\text{C}_{12}\text{H}_{13}\text{BrO}_4$ , is obtained by heating benzylideneglutaric acid with concentrated hydrobromic acid in a sealed tube at  $100^\circ$ ; it melts and decomposes at  $158-159^\circ$ , and is practically insoluble in all ordinary indifferent solvents. A. R. L.

**Synthesis of Unsaturated Dicarboxylic acids from Ketones and Diethylic Succinate.** By H. STOBBE (*Annalen*, 1894, 282, 280—319).—The synthesis of teraconic acid ( $\gamma$ -dimethylitaconic acid) by the action of sodium ethoxide on a mixture of acetone and diethylic succinate has already been described (Abstr., 1894, i, 15). The mixture of acids forming the secondary product probably contains the isomeric aticonic acid. Fittig (Abstr., 1893, i, 691) has named the acids which are formed by the action of alkalis on the itaconic acids, aticonic acids.

$\gamma$ -*Methylphenylitaconic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{COOH})\cdot\text{CMePh}$ , is prepared by the action of sodium ethoxide (2 mols.) on diethylic succinate (1 mol.) and acetophenone (2 mols.). The product is acidified, the crude crystalline mass dissolved in benzene, and carbon bisulphide added; the precipitated acid is then recrystallised from benzene or water. An isomeric aticonic acid is separated from the mother liquor (see below).  $\gamma$ -Methylphenylitaconic acid separates from water in lancet-shaped crystals, and melts and decomposes at  $161-163^\circ$ . The *barium* salt forms stellate groups of needles; the *silver* salt is a flocculent precipitate, tolerably stable towards light; and the *calcium* salt crystallises in well-formed prisms.

$\gamma$ -*Methylphenylparaconic acid*,  $\text{COOH}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CMePh}\cdot\text{O} \end{smallmatrix}$ , is obtained when  $\gamma$ -methylphenylitaconic acid is heated on the water bath with sulphuric acid diluted with an equal volume of water, or with hydrochloric acid of sp. gr. 1.15; also, when the last-named acid is treated in the cold with hydrobromic acid saturated at  $0^\circ$ . It forms stellate groups of needles, and melts at  $123-124^\circ$ . The *calcium* salt is very sparingly soluble in alcohol, and the *silver* salt is readily soluble in water.

$\gamma$ -*Methylphenyl- $\beta$ -bromoparaconic acid*,  $\text{COOH}\cdot\text{CBr}\begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CMePh}\cdot\text{O} \end{smallmatrix}$ , is obtained by brominating  $\gamma$ -methylphenylitaconic acid; it crystallises from benzene in stellate groups of needles, and melts at  $152-153^\circ$  with decomposition; when reduced with sodium amalgam, it is quantitatively converted into  $\gamma$ -methylphenylparaconic acid.  $\gamma$ -*Methylphenylaconic acid*,  $\text{COOH}\cdot\text{C}\begin{smallmatrix} \text{CH}-\text{CO} \\ \text{CMePh}\cdot\text{O} \end{smallmatrix}$ , is formed when the last-described bromo-acid is boiled with water; it crystallises in four-

sided prisms, melts at 178—179°, and is converted into  $\gamma$ -methylphenylparaconic acid when treated with sodium amalgam.

The acid isomeric with  $\gamma$ -methylphenylitaconic acid, obtained in the preparation of the latter (see above), forms needles, melts at 142—143°, and is probably *methylphenylitaconic acid*; it yields a bromolactonic acid,  $C_{12}H_{11}BrO_4$ , which melts at 175°.

By the action of sodium ethoxide on a mixture of methyl ethyl ketone and diethyl succinate, two isomerides,  $\gamma$ -*methylethylitaconic acid* and  $\gamma$ -*methylethylitaconic acid*, are formed. The latter is produced in the lesser amount, and is less soluble in ether than the former; it melts and decomposes at 165—167°.  $\gamma$ -*Methylethylitaconic acid* melts at 141—142°; the barium salt crystallises with  $3H_2O$ .

$\gamma$ -*Methylethylparaconic acid*,  $COOH \cdot CH < \begin{matrix} CH_2 - CO \\ CMeEt \cdot O \end{matrix}$ , is produced

when  $\gamma$ -methylethylitaconic acid is heated with dilute sulphuric acid; it crystallises from benzene in prisms, and melts at 125—126°.

$\gamma$ -*Methylethylbromoparaconic acid*,  $C_8H_{11}BrO_4$ , separates from water in monosymmetric crystals.  $a : b : c = 1.8275 : 1 : 1.5087$ ;  $\beta = 41^\circ 13'$ , and melts at 160—161°. If reduced with sodium amalgam, it yields  $\gamma$ -methylparaconic acid.

*Ethyl hydrogen diphenylitaconate*,  $COOH \cdot CH_2 \cdot C(COOEt) : CPh_2$ , is obtained by the action of sodium ethoxide on a mixture of benzo-phenone and diethyl succinate; it is sparingly soluble in water, and melts at 124.5—125.5°. On hydrolysis with alkali, it yields *diphenylitaconic acid*,  $COOH \cdot CH_2 \cdot C(COOH) : CPh_2$ , which melts and decomposes at 160°.

A. R. L.

**Magnesiumdiphenyl.** By F. WAGA (*Annalen*, 1894, **282**, 320—333).—The author has observed that mercurydiphenyl and magnesium powder may frequently be heated together at 200—210°, as Fleck directs (*Abstr.*, 1893, i, 622), for as long as 40 hours without any action taking place, and that the decomposition commences suddenly without carbonisation when the temperature is raised to 220°. He also finds that, when the temperature is maintained at 200—210°, the addition of a small quantity of mercuric chloride accelerates the commencement of the action. The decomposition proceeds with regularity at 180—185° if the mixture of mercurydiphenyl and magnesium is moistened with a few drops of ethylic acetate. Whereas an addition of mercury and (excess of?) magnesium is without essential influence, that of ammonium chloride and mercury phenyl chloride checks the reaction. When once the action has commenced, it should be carried to the end without intermission. The crude magnesiumdiphenyl must be treated with benzene to remove the mercury compounds with which it is contaminated; a small quantity of diphenyl and metallic mercury are produced in the reaction just described. When either magnesium powder or magnesium amalgam, moistened with ethylic acetate, is heated with diphenyl at 180—185°, no magnesiumdiphenyl is obtained.

Magnesiumdiphenyl reacts with benzoic chloride, forming benzo-

phenone; with acetic chloride, forming acetophenone; with sulphuryl chloride, forming diphenyl; with benzoic sulphochloride, forming diphenylsulphone; with arsenious chloride, forming arsenious phenyl chloride,  $\text{AsCl}_2\text{Ph}$ ; with stannic chloride, forming stannicdiphenyl chloride,  $\text{SnCl}_2\text{Ph}_2$ , which interacts with water, yielding stannicdiphenyl hydroxychloride,  $\text{Sn}(\text{OH})\text{ClPh}_2$ ; and with chloroform, forming triphenylmethane. In some cases, the reagents are mixed alone; in others the magnesiumdiphenyl is dissolved in a mixture of benzene and ether. The product of the action of magnesiumdiphenyl on carbon tetrachloride consists of a small quantity of triphenylmethane and a dark, resinous substance; whilst a colouring matter, perhaps benzaurin,  $\text{OH}\cdot\text{CPh}:(\text{C}_6\text{H}_4\cdot\text{OH})_2$ , is formed from magnesiumdiphenyl and benzotrichloride. In neither of the last two experiments was the hitherto unknown tetraphenylmethane isolated.

A. R. L.

**Diphenylsulphone Derivatives.** By O. HINSBERG (*Ber.*, 1894, **27**, 3259—3261).—Benzenesulphinic acid reacts with quinones and paranitrosamines in a similar manner to hydrochloric acid (*Ber.*, **19**, 2010).

*Paradihydroxydiphenylsulphone*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{SO}_2\text{Ph}$ , prepared from quinone and benzenesulphinic acid, forms colourless prisms which are soluble in alkalis and alkali carbonates. On oxidation, it is converted into the corresponding *quinone*,  $\text{C}_6\text{H}_3\text{O}_2\cdot\text{SO}_2\text{Ph}$ , which melts at  $196^\circ$ . The *dibenzoate* crystallises in colourless needles, melting at  $186^\circ$ .

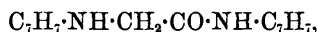
*Diphenyldisulphonedimethylparaphenylenediamine*,



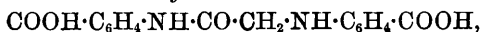
is obtained from nitrosodimethylaniline and benzenesulphinic acid; it forms slender, yellow crystals, melting at  $223^\circ$ . Mineral acids produce colourless, crystalline salts, which are decomposed by water. The *acetyl* derivative melts at about  $252^\circ$ . The amine is not acted on by hydrochloric acid at  $130$ — $140^\circ$ .

A. H.

**Synthesis of Derivatives of Indole and Glycocine.** By O. HINSBERG and J. ROSENZWEIG (*Ber.*, 1894, **27**, 3253—3258; compare *Abstr.*, 1888, 372; 1892, 1458).—Glyoxal sodium hydrogen sulphite reacts in dilute alcoholic solution with primary and secondary amines to form either glycocine or indole derivatives. Of the amines which have been hitherto used, benzylamine, piperidine, aniline, ortho- and para-toluidine, and orthamidobenzoic acid yield glycocine compounds;  $\alpha$ - and  $\beta$ -naphthylamine and ethylnaphthylamine form indole derivatives, whilst methylaniline and ethylaniline yield a mixture of the two. The following have been prepared in addition to those previously described. *Orthotoluidoacetic orthotoluidide*,



forms white, vitreous plates, melting at  $94^\circ$ , and gives crystalline salts with the mineral acids. Anthranilic acid reacts with the glyoxal solution to form the *dicarboxylic acid of anilidoacetanilide*,



which crystallises in colourless needles, melting at  $250^{\circ}$ , and does not form salts with mineral acids; this is accompanied by *orthocarboxyanilidoacetic acid*,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$ , which is soluble in hot water, and crystallises in flat prisms, melting at  $207^{\circ}$ . The same substance is also formed by the action of anthranilic acid on monochloroacetic acid. *Piperidoacetic piperidide*,  $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{NH}_{10}$ , forms large prisms, and melts at  $51^{\circ}$ ; the *platinochloride* decomposes at  $212^{\circ}$ .

*1''-Ethyl- $\beta$ -naphthindolesulphonic acid*, which has been previously described, forms a *silver salt*, which crystallises from hot water in brown needles, and decomposes at  $120^{\circ}$ . When a solution of its sodium salt is boiled with an excess of hydrochloric acid, the whole of the sulphur is eliminated, partly in the form of sulphurous anhydride, *1''-ethylnaphthindole*,  $\text{C}_{10}\text{H}_8\langle\begin{smallmatrix} \text{NEt} \\ \text{CH} \end{smallmatrix}\rangle\text{CH}$ , being formed; the latter is readily volatile with steam, and crystallises in small, white needles, melting at  $73^{\circ}$ . It gives the indole reaction, and forms a deep red colouring matter with diazobenzene chloride. *Sodium 1''-methylindolesulphonate*,  $\text{C}_8\text{H}_4\langle\begin{smallmatrix} \text{NMe} \\ \text{CH} \end{smallmatrix}\rangle\text{C}\cdot\text{SO}_2\text{Na}$ , is obtained, together with methylphenylglycocine, when methylaniline is treated with the glyoxal solution; it crystallises from water in white plates, and is not decomposed at  $300^{\circ}$ . When warmed with hydrochloric acid, it is readily converted into *1''-methyloxindole*,  $\text{C}_8\text{H}_4\langle\begin{smallmatrix} \text{NMe} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CO}$ , which crystallises in needles, melting at  $89^{\circ}$ . The sodium salt of the sulphonic acid reacts with bromine in alkaline solution to form a mixture of two isatins, which are being further investigated. Ethylaniline behaves like methylaniline. A. H.

**Tetramethyldiamidobenzhydrol.** By H. WEIL (*Ber.*, 1894, 27, 3316—3317).—When this substance is boiled with dilute mineral acids or with acetic acid, it is decomposed into dimethylaniline and dimethylamidobenzaldehyde; the latter, as well as the benzhydrol itself, condenses with the dimethylaniline to form leuco-violet.

Dimethylamidobenzaldehyde forms benzylidene compounds with primary aromatic amines even in acid solutions, a coloration or a coloured precipitate being produced; the reaction is especially delicate with benzidine compounds. C. F. B.

**Diphenylmethane Colouring Matters.** By K. ALBRECHT (*Ber.*, 1894, 27, 3294—3299).—*Tetramethyldiamidodiphenylamidocetonitrile* or *hydrocyanauramine*,  $\text{NH}_2\cdot\text{C}(\text{CN})(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , is prepared by the interaction of potassium cyanide and auramine in alcoholic solution at the ordinary temperature; it is deposited in colourless crystals, melts at  $130^{\circ}$ , and is resolved into hydrogen cyanide and auramine. The yield is 90 per cent. of the theoretical. By the prolonged action of boiling water, or more rapidly with glacial acetic acid or dilute hydrochloric acid, the nitrile is hydrolysed, ammonia is eliminated, and the resulting carbinol, in presence of zinc chloride or sodium chloride, is converted into the chloride,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{Cl}$ .

This compound is also formed by the action of nitrites on the nitrile in acid solution, and has been previously obtained by H. Weil (*Ber.*, 1884, 17, 1403) by the oxidation of tetramethyldiamidodiphenylacetonitrile; it crystallises in green needles, and, in presence of tannin, dyes cotton yellowish-green.

*Tetramethyldiamidodiphenylamidoacetamide*,



is prepared by the action of concentrated sulphuric acid on the nitrile at ordinary temperatures; it crystallises in colourless, lustrous needles, and melts at 170°. The yield is 85—90 per cent. of the nitrile employed. The compound is stable, and does not readily react with alcoholic potash or zinc dust; but by the action of acetic acid, the group  $\text{CONH}_2$  is eliminated; the resulting hydroxy-derivative is greenish-yellow. The *acetamide chloride* is crystalline and colourless.

*Tetramethyldiamidodiphenylamidoacetic acid*,



formed by the prolonged action of alcoholic potash on the acetamide, is yellow, crystalline, sparingly soluble, and melts and decomposes at 171°. With nitrous acid, auramine is regenerated. The *hydrochloride* and *sodium salt* are colourless and crystalline, and react with glacial acetic acid like the acetamide.

*Tetramethyldiamidodiphenylglycollamide*,



is obtained by the action of hydrochloric acid and zinc chloride on the acetamide; it crystallises with alcohol, and melts at 162—163°; the anhydrous, yellow crystals melt at 140—142°. With tannin as a mordant, it dyes cotton a pure greenish-blue, but the colour is unstable. The basic properties of the compound are feeble; the *salts* dissolve in water with a blue coloration, but soon dissociate. The salts of *tetramethyldiamidodiphenylglycollic acid*,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{COOH}$ , are prepared like those of the acetic acid (see above), and by the action of hydrochloric acid and zinc chloride on the amidoacetic acid; the free acid has not been isolated. The *potassium salt* crystallises in colourless, slender needles.

The replacement of hydrogen in tetramethyldiamidodiphenyl carbinol by the  $\text{CN}$ -,  $\text{CONH}_2$ -, or  $\text{COOH}$ -groups respectively, causes the colour to change from blue to green and greenish-blue, and its intensity is considerably diminished.

J. B. T.

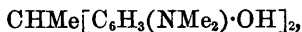
**Pyronines.** By J. BIEHRINGER (*Ber.*, 1894, 27, 3299—3305; compare R. Möhlau and P. Koch, this vol., i, 46).—The term pyronine is applied to a class of dyes formed by the condensation of aldehydes (1 mol.) with dialkylmetamidophenols (2 mols.). Dimethylmetamidophenol melts at 85°, readily dissolves in acids and alkalis, and produces mirrors with silver and gold salts. Diethylmetamidophenol resembles the dimethyl derivative, and melts at 74°. The preparation of tetramethyldiamidodihydroxydiphenylmethane from formaldehyde and dimethylmetamidophenol has been previously de-



scribed. The *hydrochloride*,  $C_{17}H_{22}O_2N_2 \cdot 2HCl + H_2O$ , crystallises in rose-coloured plates and melts at  $110^\circ$ , the *zincchloride* in needles; the *hydrochloride* of the *benzoyl* derivative crystallises in colourless needles, melts at  $141^\circ$ , and gives a blue coloration with lead peroxide.

*Tetramethyldiamidodiphenylmethane oxide*,  $CH_2:[C_6H_3(NMe_2)]_2 \cdot O$ , prepared by the action of sulphuric acid on the dihydroxy-derivative, crystallises in lustrous needles or plates, melts at  $116^\circ$ , and is rapidly oxidised by exposure to light. By the prolonged action of the acid on the anhydro-base, a compound is obtained which has a strong blue fluorescence, changing to green on the addition of acid; it is contained in the technical dye, is probably formed by the elimination of the dimethylamine group, and is being further investigated. When oxidised, the anhydro-base yields the carbinol derivative,  $OH \cdot CH:[C_6H_3(NMe_2)]_2 \cdot O$ , which closely resembles rosaniline in appearance. The alcoholic and acetone solutions are red, with a yellow fluorescence; the benzene solution exhibits no fluorescence. The *hydrochloride* crystallises in steel-blue, lustrous needles.

Ethylidenetetramethyldimetamidophenol,



forms colourless crystals melting at  $167^\circ$ , not at  $140^\circ$  as stated by Möhlau and Koch. The *benzoyl* derivative has been prepared, and gives a pale blue coloration with acetic acid and lead peroxide.

J. B. T.

**Symmetrical Orthodiamidobenzophenone.** By W. STAEDL (*Ber.*, 1894, **27**, 3362—3363).—The author has recently shown (*Abstr.*, 1894, i, 599) that the substance usually known as  $\gamma$ -diamidobenzophenone is in reality symmetrical orthodiamidobenzophenone. Since Gram has shown (*Inaug. Diss.*, Jena, 1892) that tetranitrodiphenylmethane is readily converted into symmetrical diamidoacridine, it appeared probable that the above diamido-derivative could in a similar manner be converted into acridine or acridone, and on examination this proved to be the case, although the reactions do not proceed so well as in the case of tetranitrodiphenylmethane. To obtain acridine, the diamido-compound is heated with zinc dust, whilst acridone is formed by heating it with concentrated hydrochloric acid or zinc chloride.

The author has shown in his previous paper that diamidobenzophenone is converted by nitrous acid into xanthone; at the same time an isomeric substance is always obtained, which the author regards as a *hydroxydiphenylene ketone*,  $OH \cdot C_6H_3 > CO$ , its formation being analogous to that of fluorene from orthamidodiphenylmethane (this vol., i, 52).

H. G. C.

**Preparation of Orthamidobenzophenone and Synthesis of Acridone.** By C. GRAEBE and F. ULLMANN (*Ber.*, 1894, **27**, 3483—3484).—Orthamidobenzophenone is prepared by the action of sodium hypobromite on orthobenzoylbenzamide; the yield is about 40 grams from 50 grams of phthalic anhydride. Attempts to prepare acri-

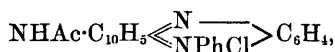
dine from this by the action of various dehydrating agents were not very successful; the best results were obtained with phosphorus chloride and calcium oxide. Acridone is formed by the action of lead oxide on orthamidobenzophenone at 350—360°; the yield is 50 per cent.

Orthohydroxybenzophenone in small, and fluorenone,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CO}$ , in large, quantity, are formed from the amidophenone by means of the diazo-reaction. The action is similar to that observed by O. Fischer and H. Schmidt, who prepared fluorene and orthohydroxydiphenylmethane from orthamidodiphenylmethane (this vol., i, 52).  
J. B. T.

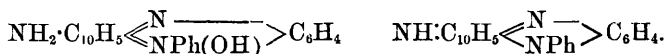
**Condensations with Formaldehyde.** By H. WEIL (*Ber.*, 1894, **27**, 3314—3316).—When formaldehyde and paranitrotoluene are allowed to remain at the ordinary temperature in solution in strong sulphuric acid, dinitroditolylmethane is formed. This must have the nitro-groups in the meta-position with regard to the  $\text{CH}_2$  group, for the only other position possible is the ortho, and this is disproved by the fact that the diamido-compound, which the dinitro-compound yields when reduced with tin and hydrochloric acid, has no tendency to form an acridine. This *diamidoditolylmethane* melts at 98—100°, and yields a *diacetyl* derivative melting at 270°.

Unlike Schöpf (Abstr., 1894, i, 600), the author has found that diphenylmethane-3:3'-dicarboxylic acid softens at 240°, and does not melt until 254°.  
C. F. B.

**Constitution of Fluorindines and Rosindulines.** By F. KEHRMANN (*Ber.*, 1894, **27**, 3348—3350).—Acetamidonaphthaquinone [ $\text{O}_2:\text{NHAc} = 1:2:4$ ] (this vol., i, 151) condenses with phenyl-orthophenylenediamine, yielding two isomeric azonium bases, the hydrochlorides of which have the formula



in which the  $\text{NHAc}$ - and  $\text{NPhCl}$ -groups are, for the two isomerides, respectively in the meta- and para-positions. The first loses acetic acid when hydrolysed, with formation of rosinduline hydrochloride, which is therefore a true azonium compound. The relation of induline to safranine is then expressed by the formulæ



C. F. B.

**Constitution of Safranines.** By C. RIS (*Ber.*, 1894, **27**, 3318—3319).—By acting on the indamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , with paramidoacetanilide, an acetylamidosafraanine has been prepared, and from this, by hydrolysis, an amidosafraanine; these exhibit the same colours as safranine itself. In a similar way an acetylamido- and an amido-dimethylsafaanine were prepared, and found to have the same colour as dimethylsafaanine. From the fact that the introduction of

a third amido-group produces no change in the colour, it is concluded that Bernthsen's symmetrical formula for safranine (Abstr., 1887, 139) is more probable than the unsymmetrical one proposed by Witt (Abstr., 1887, 250). C. F. B.

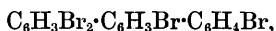
**Diphenylbenzenes.** By L. OLGIATI (*Ber.*, 1894, 27, 3385—3397).—Of the three possible diphenylbenzenes, two are at present known, namely, paradiphenylbenzene, obtained by the action of sodium on a mixture of paradibromobenzene and bromobenzene, and isodiphenylbenzene, the constitution of which is not known with certainty. It has been shown that oxidising agents partially convert it into metadiphenylcarboxylic acid, but as large quantities of paradiphenylcarboxylic acid and terephthalic acid are simultaneously formed, this affords no conclusive proof of its constitution; the author has therefore subjected the iso-compound to a fresh investigation.

For its preparation, benzene vapour was passed through a red-hot tube, and the diphenyl formed at the same time separated by fractional distillation. To separate isodiphenylbenzene from the para-derivative, the alcoholic mother liquors from the crystallisation of paradiphenylbenzene were evaporated, the residue extracted with light petroleum, the latter distilled off, the residue fractionated, and the fraction boiling at 350—400° again subjected to the same treatment. To finally remove the para-compound, the product was dissolved in carbon bisulphide and sufficient bromine added to form the monobromo-derivative, the paradiphenylbenzene remaining unchanged. The monobromoisodiphenylbenzene is extracted with light petroleum and treated with sodium amalgam and hot alcohol; on pouring the mixture into water, pure isodiphenylbenzene separates, and, after crystallisation, melts at 84—85°. It gives no trace of paradiphenylcarboxylic acid on oxidation, and is therefore free from the para-compound, whereas the product previously obtained has contained the latter in quantity, thus accounting for the presence of the para-derivatives in the oxidation products. As the subsequent investigation has shown that it is in reality the meta-derivative, the name isodiphenylbenzene need no longer be employed.

*Bromometadiphenylbenzene*,  $C_6H_5Ph_2Br$ , is obtained as described above, and forms spherical aggregates of silvery-white needles melting at 31°. On oxidation with chromic acid in acetic acid solution, it is converted into *bromometadiphenylcarboxylic acid*,  $C_{12}H_8Br\cdot COOH$ , which forms small, rhomboidal plates melting at 242°, and may be sublimed; the *barium* salt, with  $7\frac{1}{2}H_2O$ , is a crystalline precipitate, the *calcium* salt, with  $4H_2O$ , and the *silver* salt amorphous precipitates. The *methylic* salt,  $C_{12}H_8Br\cdot COOMe$ , forms feathery aggregates of short prisms melting at 67°, and the *ethylic* salt is a syrup. When the acid is treated with zinc dust and soda, it is converted chiefly into metadiphenylcarboxylic acid, thus proving that the diphenylbenzene from which it is derived is in reality the meta-derivative. Attempts to oxidise the bromometadiphenylcarboxylic acid further were not successful, total decomposition taking place; hence it is probable that the bromine atom is combined with the same

nucleus as the carboxyl group, as otherwise bromobenzoic acid would probably have been formed.

By the continued action of bromine on metadiphenylbenzene, it is finally converted into *tetrabromometadiphenylbenzene*,



which crystallises in stellate groups of slender plates melting at  $181^\circ$ , and, on oxidation, yields a mixture of bromobenzoic acids, the properties of these agreeing with those of 1 : 3 : 4-dibromobenzoic acid and parabromobenzoic acid.

*Parabromoparadiphenylbenzene*,  $\text{C}_6\text{H}_4\text{Ph} \cdot \text{C}_6\text{H}_4\text{Br}$ , is prepared by subjecting the hydrocarbon to the action of bromine vapour, and is separated by sublimation from the dibromo-compound simultaneously formed in larger quantity; it crystallises in lustrous plates melting at  $228^\circ$ , and, on oxidation with chromic acid in acetic acid solution, yields *parabromodiphenylcarboxylic acid*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , which crystallises in small needles, and may be sublimed; on reduction, it yields *paradiphenylcarboxylic acid*. *Diparabromoparadiphenylbenzene*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4\text{Br}$ , is obtained together with the monobromo-derivative, and is a heavy, white, crystalline powder melting at  $304^\circ$ . On oxidation, it yields parabromobenzoic acid in quantity, the central nucleus being destroyed, with formation of two molecules of the acid. Several salts of parabromobenzoic acid were prepared; the *lead* salt crystallises from boiling water in lustrous plates, the *cadmium* and *copper* salts are crystalline precipitates, and the *methylic* salt,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{COOMe}$ , forms volatile plates, having an odour resembling aniseed, and melting at  $74^\circ$ .

*Tetrabromoparadiphenylbenzene*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{C}_6\text{H}_4\text{Br}$ , obtained by treating paradiphenylbenzene or either of the above bromo-derivatives with an excess of bromine, crystallises in long, very thin needles melting at  $245^\circ$ ; on oxidation, it is converted into parabromobenzoic acid, but the yield is very poor. H. G. C.

**Thio-derivatives of  $\beta$ -Naphthol.** By G. TASSINARI (*Ber.*, 1894, 27, 3238).—In connection with the recent paper of Henriques on the above subject (this vol., i, 103) the author points out that he has already studied the action of the chlorides of sulphur on phenol and its homologues, and has obtained several of the compounds described by the former (*Abstr.*, 1887, 807; 1889, 245). H. G. C.

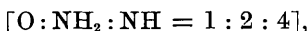
**Thio-derivatives of  $\beta$ -Naphthol.** By M. SCHILLER-WECHSLER (*Ber.*, 1894, 27, 3448—3449).—The substances described by Henriques (this vol., i, 103) as dihydroxydinaphthyl sulphide and dehydrodihydroxydinaphthyl sulphide seem to be identical with compounds, for the manufacture of which the author holds a patent (German patent, 64,816). Thiodinaphthyl oxide, identical with the dehydro-compound of Henriques, is used in certain skin diseases, and is at present being further investigated. A. H.

**Naphthazarin and the Formation of Naphthocyamic acid.** By E. SCHUNCK and L. MARCHLEWSKI (*Ber.*, 1894, 27, 3462—3465).—

The authors have been able to confirm Liebermann's view that naphthazarin is a dihydroxy- $\alpha$ -naphthaquinone, the hydroxyl groups having the position 1' : 2'. When naphthazarin is boiled with acetic anhydride, sodium acetate, and zinc dust, *tetracetyldihydroxy- $\alpha$ -naphthaquinol*,  $[(\text{OH})_4 = 1 : 4 : 1' : 2']$ , is produced. It crystallises in flat, almost colourless prisms, and melts at 277—279°. The corresponding tetrahydroxy-compound could not be isolated. The *dioxime* of naphthazarin crystallises in brownish needles, which, when heated, decompose before melting.

Naphthocyamic acid is formed by the action of potassium cyanide on  $\beta$ -dinitronaphthalene, and cannot be obtained from the corresponding  $\alpha$ -compound. A. H.

**Quinoneimides and Amidoquinones.** By F. KEHRMANN (*Ber.*, 1894, 27, 3337—3347).—When amidonaphthaquinonimide,



is boiled with water containing some ammonia, it yields hydroxynaphthaquinonimide,  $[\text{O} : \text{OH} : \text{NH} = 1 : 2 : 4]$ , together with a little amidonaphthaquinone,  $[\text{O} : \text{NH}_2 : \text{O} = 1 : 2 : 4]$ , which is found to be identical with the amidonaphthaquinone of Meerson (*Abstr.*, 1888, 1200); the latter crystallises in red needles and melts at 202—203°. If, however, its hydrochloride is heated with acetic anhydride and sodium acetate, the acetamido-derivatives of the 1 : 2- and 1 : 4-quinones are formed; the latter, under these circumstances, in larger amount.

When hydroxynaphthaquinonimide,  $[\text{O} : \text{OH} : \text{NH} = 1 : 2 : 4]$ , is reduced with stannous chloride, it yields the readily oxidisable *amidonaphthaquinol*,  $[(\text{OH})_2 : \text{NH}_2 = 1 : 2 : 4]$ . This forms a *triacetyl*-derivative,  $[(\text{OAc})_2 : \text{NHAc} = 1 : 2 : 4]$ , melting at 193°, which, on partial hydrolysis with caustic soda, yields the readily oxidisable *acetamidonaphthaquinol*,  $[(\text{OH})_2 : \text{NHAc} = 1 : 2 : 4]$ , which is oxidised by chromic mixture to red *acetamidonaphthaquinone*,  $[\text{O}_2 : \text{NHAc} = 1 : 2 : 4]$ . With orthophenylenediamine, this yields an *acetamidonaphthaphenazine* which crystallises in yellow needles and melts above 370°; it also yields a red *monoxime* (?).

Amidonaphthaquinone,  $[\text{O}_2 : \text{NH}_2 = 1 : 4 : 2]$ , undergoes a similar series of changes. When reduced it yields the readily oxidisable *amidonaphthaquinol*,  $[(\text{OH})_2 : \text{NH}_2 = 1 : 4 : 2]$ ; this yields a *triacetyl*-derivative,  $[(\text{OAc})_2 : \text{NHAc} = 1 : 4 : 2]$ , melting at 259—260°, which, on partial hydrolysis, yields *acetamidonaphthaquinol*,  $[(\text{OH})_2 : \text{NHAc} = 1 : 4 : 2]$ , readily oxidisable to yellow *acetamidonaphthaquinone*,  $[\text{O}_2 : \text{NHAc} = 1 : 4 : 2]$ ; this melts at 202°, and yields a yellow *monoxime*,  $[\text{O} : \text{NHAc} : \text{NOH} = 1 : 2 : 4]$ , decomposing at 195—200°.

C. F. B.

**Preparation of 1 : 4-Naphtholsulphonic acid.** By F. REVERDIN (*Ber.*, 1894, 27, 3458—3462).—The direct sulphonation of  $\alpha$ -naphthol invariably leads to the formation of mixtures of sulphonic acids. On the other hand,  $\alpha$ -naphthyllic carbonate, when sulphonated at a temperature of 10—20°, yields a disulphonic acid which is readily converted into 1 : 4-naphtholsulphonic acid when its solution in water is boiled. If the temperature during sulphonation rises above

20°, the disulphonaphthyl carbonic carbonate begins to decompose with formation of naphtholsulphonic acid, which at once undergoes further sulphonation. This method of preparation has been patented and is of great commercial value. Naphthyl carbonic carbonate (Burkard, *Inaug. Diss.*, Basel, 1889) is prepared by passing phosgene into a solution of naphthol in aqueous soda. It crystallises in prisms and melts at 130°.

A. H.

**Orientation in the Terpene Series.** By A. BAEYER (*Ber.*, 1894, 27, 3485—3498).—Carone, like menthone, combines with nitrosyl chloride, forming a tertiary nitroso-derivative; this is not in harmony with the constitution previously suggested (*Abstr.*, 1894, i, 535), according to which it contains a para-linking; it is probable, therefore, that it contains a trimethylene ring, and its behaviour towards hydrogen bromide and potassium permanganate are equally consistent with this view. The formula  $C_8H_7 \cdot CH < \begin{smallmatrix} CH \cdot CH_2 \\ | \\ CH \cdot CO \end{smallmatrix} > CHMe$  is suggested provisionally; it will be fully discussed in a subsequent paper. *Caroneoxime* is an oily liquid, stable towards potassium permanganate, and readily soluble in alkalis and acids. *Carylamine*,  $C_{10}H_{19}N$ , prepared by reduction of the oxime, has no characteristic odour, is stable towards potassium permanganate, and gives no precipitate with platinic chloride. The *hydrochloride* is crystalline, and is converted into the salt of an isomeric base when warmed in aqueous solution. The *benzoyl* derivative crystallises in large, flat prisms melting at 123°. Cyanic acid and phenyl cyanate yield resinous products; phenylthiocarbimide gives a crystalline compound melting at 145—146°.

*Vestrylamine* is formed by heating carylamine hydrochloride in dilute aqueous or alcoholic solution; it resembles carylamine, but readily reduces potassium permanganate solution. The *hydrochloride* is crystalline; the *benzoyl* derivative resinous. Judging from the change produced in carone by heating or by the action of sulphuric acid, vestrylamine should be the amine of carveol; attempts to prepare this compound for comparison by reduction of carveoloxime were unsuccessful; it is, however, different from dihydrocarylamine, and from *dihydroeucarylamine*, which is an oily liquid that readily reduces potassium permanganate. The *hydrochloride* is crystalline; the *benzoyl* derivative crystallises in long needles melting at 155—156°. The *platinochloride* is sparingly soluble; the cyanic acid and phenylthiocarbimide derivatives are resinous. Vestrylamine hydrochloride yields a hydrocarbon when distilled in a current of hydrogen chloride, whilst carylamine hydrochloride volatilises for the most part without change, but a little of it is converted into vestrylamine hydrochloride, which then decomposes. The crude hydrocarbon gives the sylvestrene reaction, and by means of chromic acid, or, better, with hydrogen bromide in glacial acetic acid it can be separated into two portions. The crystalline compound is *carvestrene dihydrobromide*,  $C_{10}H_{16} \cdot 2HBr$ ; it crystallises in rhombic plates and melts at 48—50°. The *dihydrochloride* crystallises from glacial acetic acid in long prisms melting at 52·5°.

*Carvestrene*, prepared by the action of quinoline on the hydrobromide, boils at 178° (corr.), smells like dipentene, becomes resinous on exposure to air, decolorises potassium permanganate solution instantaneously, and is oxidised by chromic acid at ordinary temperatures. As it has no rotatory power in chloroform solution, and gives the sylvestrene reaction, it is probably a mixture of equal molecules of *l*- and *r*-sylvestrene, and bears the same relation to *l*-sylvestrene as dipentene does to *l*-limonene; its boiling point, and the fact that the dihydrobromide and dihydrochloride have different melting points, indicates that it is not a racemic compound. The constitution of carvestrene has not yet been determined with certainty. This series of compounds is divisible into two classes—those which, like carvestrene and terpinene, are readily oxidised, but combine slowly with hydrogen bromide, and those which oxidise with difficulty but yield immediately additive compounds with hydrogen bromide, such as limonene and terpinolene; as the latter compound contains two separated double linkings, the members of the first class probably have the doubly-linked carbon atoms adjacent. It is pointed out that the author and Wallach are agreed that in dipentene the double linkings are in the positions  $\Delta^{1,3}$  or  $\Delta^{1,4}$ , from which it follows that a terpene may be optically active even in the absence of an asymmetrical carbon atom (compare Abstr., 1894, i, 252).

W. F. Proost's recent paper on the resolution of  $\Delta^{2,6}$ -dihydrophthalic acid into active components (this vol., i, 141) is also referred to; and although this result alone is insufficient to cause the rejection of the formula, the preparation of the acid by intramolecular rearrangement from the acid  $\Delta^{3,5}$  is equally compatible with the intermediate constitution  $\Delta^{3,6}$ , which contains an asymmetric carbon atom; should further investigations confirm this suggestion, the striking similarity of the compound, in chemical properties, to the acid  $\Delta^{2,4}$  will be satisfactorily explained. The orientation in the phthalic acid series is by no means so well established as in the terephthalic acid derivatives, as, owing to the great instability of many of the former compounds, several members have not yet been isolated.

J. B. T.

**Hydroxyterpenylic acid.** By O. BEST (*Ber.*, 1894, 27, 3333—3335).—A reply to some criticisms of Wallach (Abstr., 1894, i, 421).

**Pennyroyal Oil.** By T. AM ENDE (*Chem. Centr.*, 1894, i, 743).—The chief constituent of the essential oil of pennyroyal is the ketone,  $C_{10}H_{16}O$ , pulegone. Besides the oxime-like compound (m. p. 157°) obtained by Beckmann (Abstr., 1891, 936) by the action of hydroxylamine on pulegone, the normal *pulegoneoxime*, m. p. 118—119°, is obtained by adding hydroxylamine hydrochloride and alkali to an alcoholic solution of pulegone. Pulegoneoxime, when treated with dilute acids, does not yield a nitrile, but is reconverted into pulegone, and it remains unchanged when treated with phosphoric anhydride or phosphorus pentachloride. A liquid *oxime* is obtained, along with the above pulegoneoxime. *Pulegoneamine* is formed when the oxime is reduced with sodium and alcohol; it melts at 49–50°, the *oxalate* melts at 109–110°. The liquid pulegoneoxime, on reduction, yields a

mixture of the pulegoneamine, melting at 49—50° and boiling at 205—210°, and an *amine* which boils at 205—210°. Pure pulegone is obtained by decomposing pulegoneoxime with dilute sulphuric acid; it boils at 220—225°, has the refractive index  $n_D = 1.47974$  at 21°, and the sp. gr. = 0.933 at 20°.

Wallach (Abstr., 1893, i, 115) has obtained two bases, boiling at 160—170° and 250° respectively, by treating pennyroyal oil with ammonium formate. The author has obtained the same bases by the action of ammonium formate on pulegone. The base of lower boiling point, which boils at 150—151°, was identified as heptyleneamine,  $C_7H_{13} \cdot NH_2$ , and was converted into a carbamide, melting at 173°. The base of higher boiling point,  $NH(C_7H_{13})_2$ , is the secondary base corresponding with heptylamine; it boils at 275°, and solidifies in a freezing mixture. E. C. R.

**Preparation of Bromocamphoric Anhydride and of Lauranolic acid.** By O. ASCHAN (*Ber.*, 1894, 27, 3504—3508).—The unsaturated acid, obtained by the action of alkali on bromocamphoric anhydride (Abstr., 1894, i, 615), proves to be lauranolic acid; it was identified by means of the calcium and silver salts, and by the preparation of the *amide*, which crystallises in hydrated, highly-lustrous plates, melting at 72°. The *bromolactone*,  $C_9H_{13}BrO_2$ , smells like camphor and melts at 187°. Details of an improved method for the preparation of bromocamphoric anhydride are given, by which the yield is increased from 50 to 70 per cent.; the chief difference from the method already described is that only slightly more than the theoretical quantity of bromine is employed. The yield of lauranolic acid is 17 per cent. of the bromanhydride taken, in addition to the camphanic acid; the latter is converted directly into lauranolic acid by distillation under reduced pressure; the yield is about 24 per cent. together with 5 per cent. of campholactone and 10 per cent. of a hydrocarbon,  $C_9H_{14}$ , previously obtained by Wreden by heating camphanic acid with water. The relative proportions in which the three compounds are formed is largely dependent on the pressure under which the distillation is conducted; increase in this diminishes the quantity and purity of the lauranolic acid. J. B. T.

**Sulphocamphylic acid.** By W. KOENIGS and C. MEYER (*Ber.*, 1894, 27, 3465—3470).—Sulphocamphylic acid crystallises with  $3H_2O$ , two of which are lost at 100°. The third molecule is lost at 106—108°, so that the anhydrous acid has the formula  $C_9H_{11}SO_3$ . The normal *methylic salt* melts at 72°, the *monomethylic salt* at 140°. They are both formed when the normal silver salt is heated with methylic iodide and benzene under an additional pressure of a few centimetres of mercury.

Isolauranolic acid, which is obtained when sulphocamphylic acid is treated with superheated steam, is converted, by careful oxidation with permanganate, into *isolauronic acid*,  $C_9H_{12}O_3$ . This substance crystallises from hot water in yellow needles, and melts at 132°. The acid is monobasic, and forms a sparingly soluble, crystalline, *silver salt*. It contains a keto- or aldehyde-group, and reduces am-



moniacal silver oxide even in the cold. The *phenylhydrazine* compound crystallises in yellow needles, and melts at  $199^{\circ}$ ; the *semicarbazide* compound is a white, crystalline precipitate, which melts and decomposes at  $248\text{--}250^{\circ}$ . When this acid is heated on the water bath with sulphuric acid, it is converted into paraxylylic acid,  $\text{C}_9\text{H}_{10}\text{O}_2$ .

When sulphocamphylic acid is heated at  $170\text{--}180^{\circ}$  with aqueous phosphoric acid, it yields the same hydrocarbon of the formula  $\text{C}_9\text{H}_{14}$  as has already been obtained by Damsky by the distillation of ammonium sulphocamphylate with ammonium chloride. A. H.

**Synthesis of Quinoline and of Scatole.** By E. BAMBERGER and M. KITSCHOLT (*Ber.*, 1894, **27**, 3421—3427).—When the ethyl ether of monophenylglycoline is treated with phosphoric anhydride, a mixture of quinoline, scatole, and aniline is formed, accompanied by a secondary base, which is probably 1':4'-dihydroquinoline.

*Phenylglycoline ethyl ether*,  $\text{NPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OEt}$ , is prepared by warming a mixture of formanilide and dichlorhydrin in alcoholic solution with sodium ethoxide. It crystallises from light petroleum in rhombic plates, which become bluish-violet on exposure to air; it melts at  $61.5^{\circ}$ , and boils at  $217^{\circ}$  under a pressure of 40 mm. A brownish-green coloration is developed in the acid solution by potassium dichromate and by ferric chloride. The *acetyl* derivative, which is formed with elimination of  $2\text{H}_2\text{O}$ , is a pale yellow, viscous oil; the *nitrosamine* is also an oil.

*Phenylglycoline*,  $\text{NPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , is obtained on hydrolysing the ethyl ether with concentrated hydrochloric acid at  $150\text{--}155^{\circ}$ . It melts at  $52^{\circ}$  and boils at  $249^{\circ}$  (50 mm.). The solution in sulphuric acid is coloured brownish-green by potassium dichromate, whilst ferric chloride develops a yellowish-brown coloration. The *acetyl* derivative is a yellowish oil, and the *benzoyl* derivative crystallises in lustrous plates, which melt at  $113^{\circ}$ . When heated with zinc chloride at  $230^{\circ}$ , phenylglycoline yields a mixture of the above-mentioned bases. M. O. F.

**Constitution of the so-called Quinoline Ammonium Bases.** By W. ROSER (*Annalen*, 1894, **282**, 363—373, 373—385).—The experiments recorded in these papers were made to test the author's speculations (*Abstr.*, 1893, i, 177). When the methochloride of cinchonic acid is dissolved in concentrated sodium hydroxide, two compounds are formed, to which the author assigns the names methylidihydrocinchonic acid and methylquinolonecarboxylic acid. The alkaline solution is nearly neutralised with hydrochloric acid and acetic acid added to the filtrate until a precipitate no longer falls; this precipitate is *methylidihydrocinchonic acid*,  $\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{CH}$   
 $\text{NMe} \text{---} \text{CH}_2$ ; it crystallises from aqueous alcohol in minute, yellow needles, has not a sharp melting point, and dissolves in hydrochloric acid, forming a colourless solution, from which it is reprecipitated by sodium carbonate, but is redissolved by an excess of that reagent, forming a

yellow solution. The compound decomposes when kept, becoming brownish-red, and is then no longer soluble in alkalis.

*Methylquinolonecarboxylic acid*,  $C_8H_4 \begin{smallmatrix} C(COOH):CH \\ NMe \text{ --- } CO \end{smallmatrix}$ , is precipitated on adding hydrochloric acid to the filtrate from the last compound; it melts at  $246^\circ$ , and is colourless when pure. The author regards this acid as identical with the so-called methylenecinchoxinic acid (Claus, Abstr., 1892, 1490). When the silver salt is distilled in a current of hydrogen, a compound passes over, which is probably methylquinolone.

When quininic acid methochloride is dissolved in alkali, a yellowish-red solution is formed, from which hydrochloric acid precipitates *paramethoxymethylquinolonecarboxylic acid*,  $C_{12}H_{11}NO_4$ , which forms yellow needles, and melts above  $290^\circ$ ; the other product of the reaction was not investigated. The author then discusses the bearing of these results on his theoretical views.

$\alpha$ -Iodoquinoline methiodide,  $C_9NH_6I \cdot MeI$ , is prepared by heating  $\alpha$ -chloroquinoline with excess of methylic iodide in a sealed tube at  $100^\circ$ ; it gives a compound,  $C_{10}NH_9I_2 \cdot C_{10}NH_9I \cdot OEt$ , which melts at  $80-82^\circ$ , and crystallises in brown needles, having a metallic lustre. The question whether a complete conversion into  $\alpha$ -ethoxyquinoline methoxide is possible was not answered.

$\alpha$ -Iodoquinoline ethiodide,  $C_9NH_6I \cdot EtI$ , crystallises from alcohol in brown needles and melts at  $220^\circ$ ; it reacts vigorously with aniline, forming  $\alpha$ -phenylamidoquinoline methiodide,  $C_9NH_6 \cdot NHPh \cdot MeI$ , which forms yellow, lustrous crystals and melts at  $118-119^\circ$ ; the corresponding methochloride melts at  $99^\circ$ , and forms a crystalline platinochloride.

$\alpha$ -Phenylhydrazidoquinoline methiodide,  $C_9NH_6 \cdot N_2H_2Ph \cdot MeI$ , is formed by treating  $\alpha$ -iodoquinoline methiodide with phenylhydrazine; it melts at  $230^\circ$ ; the corresponding methochloride becomes dark at  $150^\circ$ . These derivatives are closely related to those described by Ephraïm (Abstr., 1891, 1509).

$\alpha$ -Amidoquinoline methiodide,  $C_9NH_6 \cdot NH_2 \cdot MeI$ , is obtained by heating  $\alpha$ -iodoquinoline methiodide with alcoholic ammonia; it melts at  $247^\circ$ , and the acetyl derivative,  $C_9NH_6 \cdot NHAc \cdot MeI$ , melts at  $213^\circ$ . The methochloride melts at  $268^\circ$ , and yields a platinochloride melting at  $268^\circ$  and a mercuriochloride melting at  $163-165^\circ$ .

$\alpha$ -Amidoquinoline ethiodide,  $C_9NH_6 \cdot NH_2 \cdot EtI$ , melts at  $232^\circ$ .

The benzenylamidoxime,  $CH \begin{smallmatrix} CH \cdot C \cdot N : CPh \\ | \\ C_6H_4 \cdot NMe \cdot O \end{smallmatrix}$ , is obtained by shaking  $\alpha$ -amidoquinoline methochloride with benzoic chloride and an alkali; it melts at  $134-135^\circ$ . The hydrochloride melts at  $198^\circ$ , and the sulphate melts at  $230^\circ$ .

$\alpha$ -Methylamidoquinoline methiodide,  $C_9NH_6 \cdot NHMe \cdot MeI$ , is obtained by treating amidoquinoline methoxide with methylic iodide; it crystallises with  $1H_2O$  in long needles, and, after crystallisation from alcohol, melts at  $160^\circ$ . The corresponding methochloride yields a crystalline platinochloride.

Dimethylamidoquinoline methiodide,  $C_9NH_6 \cdot NMe_2 \cdot MeI + H_2O$ ,

crystallises in radiating groups of needles, and melts at  $197^{\circ}$ ; when boiled with sodium hydroxide, it yields dimethylamine and methylquinoline.

A. R. L.

**Derivatives of Citrazinamide: Configuration of Aconitic acid.** By S. RUHEMANN and K. J. P. ORTON (*Ber.*, 1894, 27, 3449—3457).—The homologues of aniline react with citrazinamide in a similar manner to aniline itself. *Diorthotoluidocitrazinamidol*,  $C_{20}H_{18}N_4O_3$ , forms chocolate-brown crystals, whilst *dixylydocitrazinamide*,  $C_{22}H_{22}N_4O_3$ , is a red precipitate.

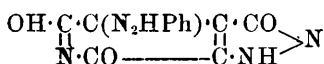
Phenylhydrazine, on the other hand (*Abstr.*, 1894, i, 260), only removes 2 atoms of chlorine, a compound of the formula



being formed.

Trichlorocitrazinamide dissolves in alcoholic ammonia with formation of an ammonium salt. When reduced with alcoholic ammonium sulphide, it is converted into *dihydrodichlorohydroxycitrazinamide*,  $NH_2 \cdot CO \cdot CH \begin{array}{c} \swarrow CCl_2 \\ \searrow CH(OH) \cdot C(OH) \end{array} \begin{array}{c} \text{---} CO \\ \text{---} \end{array} \searrow N$ , which crystallises in colourless needles and decomposes at  $98^{\circ}$ . The ammonium salt of this substance forms yellowish needles, whilst the aniline salt also forms yellow needles, decomposing at  $135^{\circ}$ .

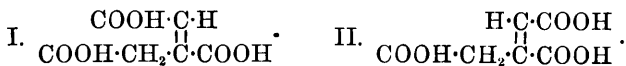
When dihydrodichlorohydroxycitrazinamide is treated with phenylhydrazine, a salt of the formula  $C_6H_4Cl_2N_2O_3 \cdot NH_2 \cdot NHPb$ , is formed, which crystallises in yellow needles and decomposes at  $145^{\circ}$ ; when this is boiled in aqueous solution with phenylhydrazine and a little acetic acid, a phenylhydrazine salt of the formula



is formed. It crystallises in reddish-brown needles, and when boiled with glacial acetic acid, a new compound,  $C_{18}H_{13}N_5O_3$ , is produced, which is the *phenylhydrazone* of *phenylpyrazolonediketohydroxypyridine*; this crystallises in red needles, decomposes at  $245^{\circ}$ , and does not reduce Fehling's solution. It is probable that when dihydrodichlorohydroxycitrazinamide is treated with phenylhydrazine, an intermediate compound of the formula  $NHPb \cdot N \cdot C \begin{array}{c} \swarrow C(CONH_2) \\ \searrow C(OH) \end{array} \begin{array}{c} \text{---} CCl \\ \text{---} N \end{array} \searrow CO$  is formed. The remaining chlorine atom is then replaced by the phenylhydrazine residue, ammonia is evolved, and the phenylhydrazine salt described above is formed. The phenylhydrazone,  $C_{18}H_{13}N_5O_3$ , is not altered by treatment with hydrochloric acid, but is converted by aqueous potash into a colourless substance,  $C_{18}H_{12}N_4O_4$ , which crystallises in needles, melting at  $245^{\circ}$  with evolution of gas. This compound is probably *phenylpyrazolonephenylpyridazonecarboxylic acid*,  $N \cdot C(COOH) \cdot C \cdot CO \begin{array}{c} \swarrow NPh \cdot CO \\ \searrow C \cdot NH \end{array} \searrow NPh$ .

Of the two possible configurations, I and II, aconitic acid seems to

have the first, as this alone can be reconciled with the formation of citrazinamide from it.



The fact that trichlorocitrazinamide does not form a pyrazolone derivative when treated with phenylhydrazine, is also in favour of this view. The second, maleïnoid, formula probably represents the constitution of aceconitic acid (Baeyer, *Annalen*, 1865, **135**, 306).

The formation of a pyrroline derivative from aconitic acid must be supposed to take place indirectly, transformation into the maleïnoid form preceding the closing of the pyrroline ring (*Trans.*, 1894, 9).

A. H.

**Scopolamine.** By F. SCHMIDT (*Arch. Pharm.*, 1894, **232**, 409—437).—In a former communication (*Abstr.*, 1892, 1255), the author showed that the so-called commercial hyoscine preparations consisted chiefly of a base of the formula  $\text{C}_{17}\text{H}_{21}\text{NO}_4$ , to which he gave the name scopolamine. As Ladenburg called this work in question (*Abstr.*, 1892, 1366), the author has again examined samples of commercial hyoscine bromide and hyoscine iodide, but in all cases has found them to consist mainly of the corresponding scopolamine salt, together with traces of salts of atropine and hyoscyamine and of another alkaloid present in too minute traces for characterisation. The author has also investigated large quantities of hyoscyamus seeds. Considerable quantities of scopolamine and hyoscyamine and small quantities of atropine were obtained from these seeds, but no hyoscine could be detected. He therefore considers the existence of hyoscine,  $\text{C}_{17}\text{H}_{23}\text{NO}_3$ , to be doubtful, although not yet fully disproved.

*Scopolamine picrate* crystallises in yellow needles melting at 187—188°, and soluble in boiling water. The *methiodide* forms colourless prisms melting at 215°, and easily soluble in water and boiling alcohol. The methiodide is not decomposed by potash, but, with moist silver oxide, yields the *methohydroxide* as a strongly alkaline, gummy, and hygroscopic mass; this reaction proves scopolamine to be a tertiary base. The *methaurochloride* forms yellow, silky needles melting at 145—146°. *Scopolamine ethiodide* forms colourless needles melting at 185—186°. *Benzoylscopolamine hydrochloride*,  $\text{C}_{17}\text{H}_{20}\text{BzNO}_4 \cdot \text{HCl}$ , was obtained as a syrup, from which the *aurochloride* was prepared as an amorphous salt melting at 161°, the *platinochloride* as an amorphous salt melting at 199—200°.

Acetic chloride is without action on either hyoscyamine or atropine, but benzoic chloride reacts with both these alkaloids. With atropine, it yields *benzoylatropine*; with hyoscyamine, according to the conditions of experiment, *benzoylhyoscyamine* or *benzoylatropine*. *Benzoylhyoscyamine aurochloride*,  $\text{C}_{17}\text{H}_{22}\text{BzNO}_3 \cdot \text{HAuCl}_4$ , is a yellow, amorphous mass melting at 70°; the corresponding *platinochloride* melts at 164—170°. *Benzoylatropine aurochloride*,  $\text{C}_{17}\text{H}_{22}\text{BzNO}_3 \cdot \text{H} \cdot \text{AuCl}_4$ , is a yellow, amorphous, and gummy mass melting at 125—135°; the corresponding *platinochloride* melts at 215°. When hyoscyamine or

atropine is heated with acetic anhydride and a little sodium acetate, no acetylation occurs, but both the alkaloids are converted, by the abstraction of the elements of water, into apoatropine. Under like conditions, scopolamine appears to be partly acetylated, partly converted into an apo-derivative, but the products could not be fully isolated. When an aqueous solution of scopolamine hydrobromide is treated with moist silver oxide, it is in part converted into an almost inactive *scopolamine*, which crystallises (more easily than the ordinary scopolamine) in needles melting at  $55-56^\circ$ , and yields an *aurochloride* closely resembling that of the ordinary alkaloid. The *hydrobromide* is much more readily crystallisable than that of the normal alkaloid, and forms colourless, crystalline aggregates, showing a rotation  $[\alpha]_D = +0.44^\circ$  as compared with  $[\alpha]_D = -25^\circ 43'$  for normal scopolamine hydrobromide. This inactive scopolamine is still under investigation.

Scopoline, which is now being investigated, is a tertiary base, which is oxidised by barium permanganate to a secondary base,  $C_7H_{11}NO_2$ ; the latter yields a crystalline *nitroso*-derivative, but is reconverted into scopoline by the action of methylic iodide.

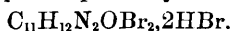
L. T. T.

**Identity of Sophorine and Cytisine.** By P. C. PLUGGE (*Arch. Pharm.*, 1894, **232**, 444—460).—Considerable quantities of sophorine were extracted from *Sophora tomentosa*, and very carefully compared with pure cytisine,  $C_{11}H_{14}N_2O$ , with the result that these two alkaloids proved to be identical. During this investigation, many new characteristics of cytisine were determined, and new derivatives formed.

The rotary polarisation of cytisine nitrate is  $[\alpha]_D = -93^\circ 26'$ , the coefficient of refraction, 1.34449. Cytisine gives no reaction with strong sulphuric acid, or with that acid and sugar, cerous oxide, or vanadic acid. Fröhde's reagent, and evaporation with phosphoric acid, likewise yield no reaction. Erdmann's reagent causes an orange-yellow coloration; concentrated nitric acid, on warming, a reddish-yellow coloration, which becomes rather darker on the addition of potash; strong sulphuric acid and potassium dichromate, a green coloration; evaporation with hydrochloric acid leaves a yellow residue; calcium hypochlorite gives no coloration.

*Methylcytisine hydriodide*,  $C_{12}H_{16}N_2O, HI$ , prepared by the action of methylic iodide on the free alkaloid, yields colourless crystals; its solution gives a rotary polarisation,  $[\alpha]_D = -81^\circ$ , and a refractive index of 1.35427. The *platinochloride* crystallises in orange-yellow needles; the *aurochloride* in golden-yellow needles.

With bromine, cytisine yields an orange-red compound containing 4 atoms of bromine, 2 of which are removed by digesting it with silver nitrate. The compound probably has the formula



The author claims priority for his pupil, van de Moer, in establishing the identity of sophorine with cytisine.

As both ulexine and sophorine are now proved to be identical with cytisine, this alkaloid has been shown to be present in the various

species of *Cytisus*, in *Ulex europaeus*, and in *Sophora tomentosa*. Haage and Schmidt failed to find it in *S. japonica*, *S. jap. pendula*, and *S. affinis*, but it is probably present in the poisonous species *S. speciosa* and *S. secundiflora*.  
L. T. T.

**Alkaloids from the Root of Pomegranate Root.** By G. CIAMICIAN and P. SILBER (*Ber.*, 1894, **27**, 2850—2861; compare *Abstr.*, 1894, i, 154).—Norgranatanine (*loc. cit.*) is best obtained by heating granatoline with phosphorus and hydriodic acid for 6—8 hours at 260°, and is separated by means of the carbamate, which melts at 135—136°; the base forms colourless needles melting at 50—60°, and the *platinochloride* separates in yellow plates which melt at 255°. The *nitroso-derivative*,  $C_8H_{14}N \cdot NO$ , melts at 148°. The *benzoyl derivative* forms colourless needles, which melt at 111°. When the dry hydrochloride is distilled with excess of zinc dust,  $\alpha$ -propylpyridine is formed, the behaviour of norgranatanine under these circumstances being identical with that of  $\gamma$ -coniceine.

*Norgranatoline*,  $C_8H_{15}NO$ , is obtained by the oxidation of granatoline with potassium permanganate in alkaline solution; it crystallises in needles or colourless prisms, and melts at 134°. The *hydrochloride* is hygroscopic, and the *aurochloride* melts at 215°. The *nitroso-derivative* forms colourless plates, which retain water and melt at 72—73°; in the anhydrous condition it melts at 125°. Pyridine is produced by the distillation of norgranatoline hydrochloride with zinc dust.

*Norgranatenine*,  $C_8H_{13}N$ , is formed on reducing norgranatoline with phosphorus and hydriodic acid. The *carbamate* melts at 104—106°, the *hydriodide* at 221°, the *hydrochloride* at 250°, and the *aurochloride* at 186°. The *platinochloride* crystallises in reddish-yellow plates, which do not melt below 260°.

The probable constitutions of some of these substances are also discussed.  
M. O. F.

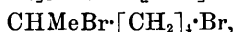
**A New Decomposition Product of Keratin.** By S. G. HEDIN (*Zeit. physiol. Chem.*, 1894, **20**, 186—192).—By methods similar to those employed by Drechsel in the preparation of lysine and lysatinine, a new base of the formula  $C_6H_{14}N_4O_2$  was obtained from horny substances; it has the same formula, and is probably identical with arginine, prepared by Schulze and Steiger from etiolated lupin seedlings. The following compounds were prepared in a crystalline form.  
(1)  $AgNO_3, C_6H_{14}N_4O_2 + \frac{1}{2}H_2O$ ; (2)  $AgNO_3, C_6H_{14}N_4O_2, HNO_3$ ; (3)  $C_6H_{14}N_4O_2, HNO_3 + \frac{1}{2}H_2O$ ; and (4)  $Cu(NO_3)_2, 2C_6H_{14}N_4O_2 + 3H_2O$ .  
W. D. H.

## Organic Chemistry.

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**Methyltrimethylene.** By N. DEMYANOFF (*Ber.*, 1895, **28**, 21—24).— $\beta$ -Butyleneglycol was prepared by reducing aldol with sodium amalgam; it was then converted, by treatment with hydrobromic acid, into dibromobutane,  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ , and this was heated with zinc dust and alcohol, when *methyltrimethylene*,  $\text{CHMe} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , was formed. This is a gas which burns with a smoky flame; it can be condensed to a liquid, which boils at  $4-5^\circ$ , and has sp. gr. =  $0.6912$  at  $-20^\circ/0^\circ$ , =  $0.6760$  at  $-8^\circ/20^\circ$ . It does not decolorise permanganate, nor does it unite with bromine in the dark; in diffused light it unites slowly with bromine, in direct sunlight instantaneously, forming the above-mentioned dibromobutane. It unites with concentrated hydriodic acid, forming secondary iodobutane; concentrated sulphuric acid absorbs and polymerises it, but the dilute acid ( $1:\frac{1}{2}$  of water by vol.) converts it, in part, at least, into butylic alcohol.

The compounds  $\text{Br}\cdot[\text{CH}_2]_4\cdot\text{Br}$ ,  $\text{Br}\cdot[\text{CH}_2]_5\cdot\text{Br}$ , and



when treated with zinc dust and alcohol, behave in a different way, and yield monobromo-derivatives of the hydrocarbons.

C. F. B.

**Reduction of solid  $\alpha$ -Dichloroethylic Cyanide.** By J. TROEGER (*J. pr. Chem.*, 1894, [2], **50**, 446—460).—The author has re-examined the reduction of solid  $\alpha$ -dichloroethylic cyanide, which was first investigated by Otto and Voigt (*Abstr.*, 1887, 1024). The first product of reduction is trimolecular *monochlorethylic cyanide*,  $(\text{CHMeCl}\cdot\text{CN})_3$ , an oil which decomposes when distilled, but is slowly volatile with steam. The base,  $\text{C}_9\text{H}_{16}\text{N}_2$ , which Otto and Voigt obtained in addition to triethylic cyanuride, is a reduction product of the latter, from which it is formed by the addition of 1 atom of hydrogen, accompanied by the loss of 1 atom of nitrogen in the form of ammonia.

The base, therefore, probably has the constitution  $\begin{smallmatrix} \text{CEt}\cdot\text{N} \\ | \\ \text{CEt}\cdot\text{N} \end{smallmatrix} > \text{CHEt}$ ,

the relation between it and triethylic cyanuride being similar to that between cyanophenin and lophine (Radziszewski, *Abstr.*, 1882, 1063). The *aurochloride* of the base forms lustrous, golden needles, and melts at  $162-165^\circ$ . The *picrate* melts at about  $130^\circ$ . The base gives many of the characteristic reactions of the alkaloids. It combines with silver nitrate to form a double compound,  $2\text{C}_9\text{H}_{16}\text{N}_2\cdot\text{AgNO}_3$ , which melts at  $122^\circ$ . When this is again treated with silver nitrate, a second double compound,  $2\text{C}_9\text{H}_{16}\text{N}_2\cdot 3\text{AgNO}_3$ , is formed.

A. H.

**Influence of Configuration on the Action of Enzymes.** By E. FISCHER (*Ber.*, 1894, **27**, 3479—3483).—The extract prepared by digesting pure, fresh, Froberg yeast for 20 hours with water

(5 parts) at 35° has no appreciable influence on maltose or on  $\alpha$ -methylglucoside. The liquid contains but little matter which is precipitable by alcohol or by boiling; it is, nevertheless, capable of inverting 10 per cent. of its weight of saccharose in 24 hours. Whether the extraction of invertase from very active yeast fails, under these conditions, as observed by O'Sullivan (Trans., 1892, 593) in the case of English high-fermentation yeast, has not been ascertained. When the same yeast (Frohberg type) is ground with powdered glass, the aqueous extract then also hydrolyses maltose and  $\alpha$ -methylglucoside, but the action is very feeble, for only 15 per cent. of the glucoside was found to be hydrolysed by 10 parts of the extract in 20 hours at 35°. If, however, a mixture of  $\alpha$ -methylglucoside (2 parts), water (20 parts), fresh Frohberg yeast (1 part), and chloroform (1 part) is kept at 35° for three days, fermentation does not occur, but 40 per cent. of the glucoside is hydrolysed. The same result was obtained with maltose.

It is known that water extracts invertase from dried yeast much more readily than from fresh yeast; this also applies to the maltose enzyme. The yeast is allowed to remain in a thin layer, at the temperature of the room, for some days, until it can be pulverised; in this condition it may be kept for a long time. The dried and pulverised yeast is digested with 20 parts of water at 30–35° for 20 hours, and the extract filtered; for this purpose, a Pukall's clay filter may be used. It was with such an enzyme solution that the former experiments (this vol., i, 6) were made, as also those to be described. The precipitation of the maltose enzyme from this solution is much more difficult than that of invertase. If double the volume of alcohol is added, a flocculent precipitate is formed, which, when quickly filtered and dried on a tile in a vacuum, is found to represent 0.5–1 per cent. of the liquid. The solution of this substance in water (25 parts) hydrolyses maltose and  $\alpha$ -methylglucoside, but the hydrolytic power is reduced by 4 per cent. as compared with the original solution.

There is a possibility that a single enzyme might have the power, in virtue of the presence of two different atomic groupings within its molecule, of hydrolysing both saccharose and maltose, and that the latter function might be arrested by the action of alcohol (compare Röhmman, this vol., i, 52). The circumstance that by extracting the fresh yeast with water, in which case no arrest of hydrolytic function is conceivable, the saccharose enzyme (invertase) alone is extracted, favours the view that two enzymes are contained in yeast. As to the nature of the second enzyme, little can be said; Röhmman's view, that it is identical with Geduld's glucase (from maize), is misleading, and is also opposed to the fact that the latter observer purified his enzyme by repeated precipitation with alcohol. It bears a closer resemblance to Röhmman's maltose-hydrolysing enzyme from blood, but the identity of the two must remain an open question. The author considers it probable that a large number of maltose-hydrolysing enzymes exist, as there are likewise many enzymes of the type of diastase, and, in order to prevent confusion, it is well to indicate the origin of the enzymes by a prefix, as, for example, yeast-glucase.

Besides Frohberg yeast, the author finds that yeast of the Saaz



type, as well as high-fermentation yeast—the so-called distillery yeast—contains a maltose-hydrolysing enzyme.

Neither fresh nor air-dried milk-sugar yeast gives, on extraction with water at  $30^{\circ}$ , a solution capable of hydrolysing milk sugar. If, however, the air-dried yeast is carefully ground with powdered glass, and extracted, the liquid obtained hydrolyses milk sugar to the extent of about one-half, and the hexoses formed may be isolated as osazones. The extract of this yeast thus falls short in hydrolytic power, in comparison with that of Kephir grains (Abstr., 1895, i, 7).

Having thus proved the existence of a lactase, the author concludes that, in the fermentation of milk sugar, and, indeed, of every polysaccharide, conversion into simple sugars precedes fermentation. The hydrolysis to simple sugars will generally occur within the yeast cells, as the specific enzymes are retained by the living individuals. Milk-sugar yeast also contains an enzyme which hydrolyses saccharose.

Kephir-lactase and the lactase from milk-sugar yeast hydrolyse neither methylgalactoside nor  $\beta$ -methylglucoside, and no benzaldehyde is formed by their action on amygdalin.

Beer yeast-glucose does not act on methylmannoside (from *d*-mannose), nor on methylsorbose. Methylfructoside (from *d*-fructose, the configuration of which is similar to ordinary glucose) is, however, readily hydrolysed; but invertase is without action on it.  $\alpha$ - and  $\beta$ -Methyl-*l*-glucosides are not attacked by beer yeast-glucose.

Emulsin does not act on methyl-*d*-mannoside, methylsorbose,  $\alpha$ - and  $\beta$ -methyl-*l*-glucosides, or methylgalactoside. The same applies to lactobionic acid and its calcium salt, although the similarity of this acid to milk sugar would have suggested the contrary.

Myrosin hydrolyses neither  $\alpha$ - nor  $\beta$ -methyl-*d*-glucoside.

A. R. L.

**Decomposition of Glucose by Alkalis.** By F. GAUD (*Compt. rend.*, 1894, 119, 604—606).—The method described by Causse of limiting the oxidising action of nitric acid on glycerol, by adding a metallic oxide which will form an insoluble salt with the acid produced, is capable of general application, and has been applied by the author to the investigation of the action of alkalis on glucose.

When glucose is treated with alkaline cupric oxide, the greater part is oxidised to tartronic acid, together with small quantities of formic and oxalic acids, but a small portion of the glucose is, at the same time, attacked by the alkali alone, with production of lactic and oxalic acids, phenols, two isomerides of dihydroxyphenylpropionic acid, and, when the glucose is in excess, melassic and glucic acids, constituting the greater part of the resinous products.

The first action of the alkali on glucose produces glucic acid by simple dehydration, but this acid splits up completely into catechol and gluconic acid, the latter in its turn yielding lactic and glyceric acids, whilst the glyceric acid, in presence of the alkali, is converted into lactic and oxalic acids. Interaction between the lactic acid and catechol produces the two isomerides,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}\cdot\text{Me}\cdot\text{COOH}$  and  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{CH}\cdot\text{Me}(\text{OH})$ . Only the hydroxyphenyl acids,

oxalic acid, and lactic acid and its ethereal salts remain when the action is complete. In order to isolate the intermediate products, the employment of various metallic oxides is necessary, the action being then limited to the formation of the particular acid. It is essential that the copper oxide should remain in solution, and this is secured by adding a small quantity of ammonia, which has no effect on the action of the other alkali. Lead hydroxide precipitates glucic and gluconic acids; cadmium hydroxide also precipitates gluconic acid; stannous chloride precipitates lactic acid, bismuth hydroxide, glyceric acid.

C. H. B.

**Action of Phloroglucinol on Sugars.** By C. COUNCLER (*Ber.*, 1895, **28**, 24—28).—Hydrogen chloride was passed into a cooled aqueous solution containing phloroglucinol (1 mol.) and a hexose or pentose (1 mol.). The product, precipitated with water in the case of the hexoses, in the case of the pentoses with alcohol, was dried on a porous plate, and finally washed with alcohol, or dissolved in alcohol and precipitated, and then washed with ether. The substances thus obtained were yellow, red, or green, the colour depending partly on the state of subdivision; they are only slightly soluble in water. They may be regarded as formed from 3 mols. of phloroglucinol and 3 mols. of the sugar with elimination of water; the number of water molecules eliminated is then, in the case of arabinose and xylose, 6; galactose and mannose, 8; dextrose, 9; and levulose, 10.

C. F. B.

**Two Remarkable Decomposition Products of Saccharose.** By E. O. v. LIPPMANN (*Ber.*, 1894, **27**, 3408—3409).—A disused conduit, formerly employed for "clairce," was taken to pieces, when the inner portions of the tubes were found to be incrustated with a thick, black, tasteless, and odourless deposit, having all the properties of the so-called humous matter. This substance had apparently been formed by gradual deposition from the pure sugar solution (clairce) remaining in the tubes at a temperature of 35—40°. Alcohol extracted a crystalline substance from the mass, which, after repeated recrystallisation from that solvent, fractional precipitation with basic lead acetate, and treatment with animal charcoal, was separable into mellitic acid and pyromellitic acid.

A. R. L.

**Maltol.** By H. KILIANI (*Ber.*, 1895, **28**, 34; compare this vol., i, 80).—Maltol is obtained in monosymmetric crystals;  $a : b : c = 0.5902 : 1 : 0.3996$ .  $\beta = 70^\circ 33' 40''$ .

M. O. F

**Methylenitan and Formose.** By O. LOEW (*Pflüger's Archiv*, 1894, **59**, 276—278).—It is pointed out that Araki (*Abstr.*, 1894, ii, 388) has fallen into error in supposing that Butlerow's methylenitan is the same thing as Loew's formose; the former contains 4 per cent. more carbon than the latter. There is also a question of priority with E. Fischer in regard to the description of the properties of formose. Loew was the first to recognise the formation of true sugars from formaldehyde by condensation.

W. D. H.

**$\beta$ -Lævulin.** By E. SCHULZE and S. FRANKFURT (*Ber.*, 1894, **27**, 3525—3527).—The crystalline lævulin obtained from unripe rye (*Abstr.*, 1894, ii, 155) has now been prepared in larger quantity. The product obtained differed in many respects from that previously described, which was apparently contaminated with saccharose.  $\beta$ -Lævulin is not converted into glucose by invertase as previously stated; it is lævorotatory, the specific rotatory power in 10 per cent. aqueous solution being  $[\alpha]_D = -28.6$  to  $-28.9$ . It is very soluble in water, and alcohol precipitates it from the concentrated aqueous solution in the form of minute prisms. The elementary analysis of the substance dried at  $100^\circ$  agrees better with the formula  $C_{16}H_{32}O_{16}$  than with  $C_{12}H_{22}O_{11}$ . On hydrolysis with dilute sulphuric acid, levulose is formed. The authors propose the name *secalose* instead of  $\beta$ -lævulin.

A. R. L.

**Steeping ("Quellung") of Starch.** By H. RODEWALD (*Landw. Versuchs. Stat.*, 1894, **45**, 201—227).—Dry starch, when placed under cold water or exposed to aqueous vapour, combines with a certain amount of water, and increases slightly in specific gravity. Flückiger showed that starches from different sources have different specific gravities (*Zeit. anal. Chem.*, **5**, 305; compare also Dietrich, *ibid.*, **5**, 51, and Kopp, *Annalen*, **35**, 38). In the present experiments, starch of one kind (wheat) was employed; it was purified by levigation, the water being removed by alcohol and the alcohol by ether. Two products (A and B) were obtained. The specific gravity was determined in air by means of a special volumeter (described with sketch), also under chloroform and under ether. The average of 12 specific gravity determinations (in air) was found to be, for A, 1.5072, of these determinations for B, 1.490. In the remaining experiments, A alone was employed. The following constants were obtained.

Sp. gr. of steeped starch.....	1.6122
Sp. vol. of dry starch.....	0.6635
Sp. vol. of steeped starch .....	0.6203
Amount of water taken up in steeping.....	0.326
Sp. heat of dry starch.....	$14.2 \pm 0.234$ cal.
Sp. heat of steeped starch.....	$0.3728 \pm 0.008974$
Steeping heat.....	23.4 cal.

It is difficult to ascertain the experimental error in determining the steeping heat; the result is probably low; pressure has no great influence on the steeping heat. The effect of temperature on the steeping heat and on the amount of water absorbed is also discussed. As regards the relations between pressure and decrease of volume in steeping, it is calculated that the shrinking of 1 gram of starch is equivalent to a pressure of 2523 atmospheres. If the shrinking (0.0432 c.c.) is assumed to take place in the 0.326 gram of water absorbed, the shrinkage for 1 gram of water would be 0.1325 c.c. This number, divided by the compression-coefficient of water (0.00004695; compare Wüllner's, *Lehrb. d. Exper.-physik.*, **1**, 275), gives 2821 atmos.

The amount of force developed by starch in steeping is measured by multiplying the decrease of volume per gram (0.0432 c.c.) by the

pressure, as calculated above (2605 kilos.); the maximum amount of force developed by 1 gram of starch in absorbing the greatest amount of water is 1.125 kilos. 11.33 per cent. of the steeping heat may be converted into work.

N. H. J. M.

**Carbohydrates of Yeast.** By E. SALKOWSKI (*Ber.*, 1894, 27, 3325—3329).—In the preparation of yeast gum (*Abstr.*, 1894, i, 222) by boiling pressed yeast with 3 per cent. aqueous potassium hydroxide, a residue is obtained, which, after it has been treated successively with water, dilute hydrochloric acid, again with water, alcohol, and ether, and finally extracted with ether in a Soxhlet's apparatus to remove fat, consists of an impure cellulose. If the yellowish powder thus obtained is heated in a digester with a large quantity of water under a pressure of 2—2.5 atmcs. for 20 hours, about half is dissolved. The solution gives an intense, brownish-red, iodine reaction, whereas the residue does not give any coloration with iodine. These two substances are accordingly denoted by the author *A-cellulose* and *B-cellulose*, or *erythrocellulose*, and *achroocellulose* respectively. When the solution is evaporated to one-fifth, almost the whole of the achroocellulose separates as a jelly, and if the filtrate is mixed with absolute alcohol, the precipitate dehydrated with alcohol and ether, and heated at 110—120°, erythrocellulose is obtained, and may be purified by again extracting with water and repeating the operations just described. It dissolves in water with a slight opalescence, and has a specific rotatory power of  $[\alpha]_D = +173.7^\circ$ . Analyses point to the formula  $C_6H_{10}O_5$ , but the substance seems to contain some combined water. On treatment with dilute acids, glucose is formed; saliva also saccharifies it, although the latter acts somewhat more slowly than it does on glycogen. In many points it resembles glycogen, but the opalescence of its solution is less, and would even seem to be due to traces of impurity. The views of Errera (*Abstr.*, 1885, 1151) and of Laurent (*Annal. de l'Institut Pasteur*, 1889, 3, 113), that glycogen is present in yeast are, in the author's opinion, without sufficient foundation. The author has already observed that the aqueous extract of yeast contains the carbohydrate giving the iodine reaction, and it seems not improbable that this exists in the yeast cells in the dissolved form; the erythrocellulose may be a carbohydrate from which cellulose is formed, or it may be a transformation product of the latter. Cremer has recently stated (*Med. Wochensch.*, 1894, No. 26) that yeast glycogen can be prepared from yeast by Brücke's method (using potassium mercuric iodide), but the author has failed to confirm this observation.

The achroocellulose mentioned above was obtained as a jelly-like mass, which remained unaltered when treated with alcohol. If dried in the water bath, a horny mass was left which could only be pulverised with difficulty. The substance seems not to be homogeneous, for on treatment with acids it yields both glucose and mannose.

A. R. L.

**Chitin and Cellulose.** By F. HOPPE-SEYLER (*Ber.*, 1894, 27, 3329—3331).—Referring to Winterstein's paper (this vol., i, 80), the author states that he has been engaged for some years in an investigation of the cellulose-like carbohydrates from plants and animals.

Tunicin, from the Tunicata, when heated with potassium hydroxide at  $180^{\circ}$ , behaves as ordinary cellulose, but chitin from articulated animals (the shells of crabs, scorpions, and spiders were examined), when so treated, although it undergoes no alteration as far as its texture is concerned, is found, after being washed free from alkali, to be readily soluble in dilute acetic acid, forming a solution from which alkali throws down a flocculent precipitate. The percentage of nitrogen in the chitin remains unaltered after this treatment, but from the alkali with which the chitin had been fused, acetic acid was isolated. The author proposes the name *chitosan* for the transformation product of chitin, soluble in acetic acid; it has basic properties, and the *hydrochloride* forms quadratic crystals, soluble in water. When chitosan is treated with concentrated hydrochloric acid it, like chitin, yields glucosamine. If heated with acetic anhydride, it yields a substance resembling chitin, which, when heated with potash at  $180^{\circ}$ , is resolved into chitosan and acetic acid. Chitosan and propionic anhydride also yield a substance resembling chitin.

Cellulose, when fused with potassium hydroxide at  $180^{\circ}$ , remains intact, but at  $200^{\circ}$  it undergoes decomposition. A. R. L.

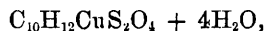
**Decomposition of Chitin.** By F. HOPPE-SEYLER (*Ber.*, 1895, 28, 82).—The conversion of chitin into chitosan and acetic acid by fusion with potash, and the formation of acetic acid and glucosamine by the action of hydrochloric acid on chitosan, are in complete accord with Schmiedeberg's view of the constitution of chitin. Chitosan easily combines with various substances, and is usually readily regenerated by the action of alkalis. The products of the interaction of acetic anhydride and chitosan are quite different from those yielded by chitin under similar circumstances, and will be described later. J. B. T.

**Production of Gaseous Formaldehyde for Disinfecting Purposes.** By R. CAMBIER and A. BROCHET (*Compt. rend.*, 1894, 119, 607—609).—Trioxymethylene is very easily obtained by mixing the commercial 40 per cent. solution of formaldehyde with about one-fourth its volume of sulphuric acid. When heated alone, trioxymethylene readily volatilises, but condenses entirely as trioxymethylene. In presence of air, however, the formaldehyde remains as such in a proportion which increases with the quantity of air present. Twenty litres of air, into which a few centigrammes of trioxymethylene has been volatilised, remains antiseptic even after eight days. The volatilisation of trioxymethylene from hot plates heated at  $200^{\circ}$  is not very satisfactory, because admixture with air takes place slowly. The authors have, therefore, employed Hofmann's reaction for the production of gaseous formaldehyde, the apparatus consisting of a reservoir and a burner. The burner consists of a block of asbestos containing a metallic tube, pierced in its upper part with a number of holes, and covered with a large D of platinum gauze. The supply of oxygen is controlled by a regulator similar to that of a Bunsen burner; this regulator is surmounted by a plate of mica forming a chimney. C. H. B.

**Valeraldehyde.** By L. BOUVEAULT and L. ROUSSET (*Bull. Soc. Chim.*, 1894, [3], **11**, 300—302).—The ordinary method of oxidising amylic alcohol to valeraldehyde, by allowing it to flow into hot chromic acid mixture, gives a very poor yield, the major part of the product consisting of isobutaldehyde and acetone, from which it is difficult to separate the valeraldehyde. The authors prefer to add the oxidising mixture to the alcohol, thus avoiding the exposure of the newly-formed aldehyde to the risk of further oxidation. The alcohol (1000 grams) is heated on the water bath in a two-necked flask, through one neck of which the oxidising mixture (sodium dichromate 1100, sulphuric acid 900, water 2250 grams) is allowed to flow, whilst the aldehyde vapour passes off through the other. The oily distillate is separated from the accompanying water, dried over fused sodium acetate, and the aldehyde distilled from unchanged alcohol. The yield is 60 per cent. on the alcohol employed. The last traces of water can be removed by means of acetic anhydride, a desiccating agent which the authors have used with advantage in drying other aldehydes, as well as ketones and a terpene. A further quantity of unchanged amylic alcohol can be recovered from the residue in the flask, in which amylic valerate and a resinous substance are also formed during the oxidation. JN. W.

**Action of Sulphur Chloride on the Copper Derivatives of Acetylacetone and Benzoylacetone.** By V. VAILLANT (*Compt. rend.*, 1894, **119**, 647—650).—When the copper derivative of acetylacetone is dissolved in chloroform, and a solution of sulphur chloride in chloroform is added drop by drop until the blue colour of the liquid disappears, cuprous chloride and sulphur are precipitated, and the liquid, on evaporation, yields a compound,  $C_{10}H_{14}S_2O_4$ , which crystallises readily in beautiful, rhombic crystals, highly refractive and of an amber-yellow colour, with the faces  $g_1$ ,  $h_1$ ,  $me$ , and  $op^{1/2}$ . It is quite insoluble in cold water, but dissolves slightly in boiling water, and is only slightly soluble in alcohol, but dissolves readily in ether, benzene, and especially chloroform. It melts at 90—91°, and readily remains in superfusion; when heated in presence of air, it decomposes without boiling. Fuming nitric acid attacks it with almost explosive energy, and potassium permanganate, in presence of light petroleum, yields a crystalline compound which has not yet been analysed.

The sodium derivative,  $C_{10}H_{12}Na_2S_2O_4$ , is obtained by the action of sodium on a solution in dry ether; it crystallises with difficulty, and dissolves in water, but is decomposed on boiling. The copper derivative is obtained by the action of copper acetate on the sodium compound, or on an ethereal solution of the substance itself; it crystallises, with some difficulty, from chloroform in small, dark green octahedra. When dried at 60°, it has the composition



and at 100°, it decomposes.

It will be observed that since the product is a dithio-derivative, the action of sulphur chloride on acetylacetone is not analogous to

its action on ethylic acetoacetate. The dithio-derivative has already been obtained by C. and A. Combes by the action of sulphur chloride on acetylacetone.

The copper derivative of benzoylacetone, when treated with sulphur chloride, yields dithiobenzoylacetone, which crystallises in the rhombic system; it forms a copper compound, and gives a red coloration with ferric chloride.

C. H. B.

### Action of Methylic Bromopropionate on Sodium Nitrite.

By G. LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], 11, 297—300).—*Methylic α-bromopropionate* is prepared in the same way as the ethylic salt (Abstr., 1893, i, 65), namely, by heating propionic acid with bromine and sulphur, and subsequently heating the crude bromopropionic acid thus formed with methylic alcohol and concentrated sulphuric acid. The yield of crude product is 91 per cent., and, on fractionation, more than half this quantity is obtained as a colourless liquid boiling at 145—150°, and having a sp. gr. of 1.5 at 15°.

When methylic α-bromopropionate is gently heated with methylic alcohol (1 vol.) and sodium nitrite (2 mols.) (compare Abstr., 1894, i, 114), a deep red colour is gradually developed, and carbonic anhydride, nitrogen, and nitric oxide are evolved. The portion of the product insoluble in water consists of a heavy, yellowish oil, which solidifies on agitation, and, on recrystallisation from methylic alcohol, forms a brilliant, white saccharoidal mass of clinorhombic prisms; it melts at 64°, and then remains in a state of superfusion. Its composition corresponds with that of *methylic dinitrosolactate*,  $[\text{COOMe}\cdot\text{C}(\text{NO})\text{Me}]_2\text{O}$ , and it is accordingly hydrolysed by baryta water into acetic acid, hydroxylamine, and carbonic anhydride. The soluble portion of the product contains a small quantity of *methylic α-nitrosopropionate*, which crystallises in small, silky needles from the ethereal extract, and melts at 69°. The *silver* salt forms a white precipitate, and is anhydrous. Sodium ethylnitrolate and sodium acetate also appear to be present.

The author considers that the immediate product of the action between the bromopropionate and the nitrite is methylic α-nitropropionate, and that the substances mentioned above are formed from this by secondary changes. Part condenses to the dinitrosodilactate, and another part is converted into the nitrosopropionate, but the bulk is decomposed by the excess of sodium nitrite into carbonic anhydride and sodium nitrolate; the formation of the latter accounts for the development of the red colour. The nitrolate is in turn decomposed to some extent into sodium acetate and a mixture of nitrogen and nitric oxide, which, with the carbonic anhydride just mentioned, constitute the gases evolved.

JN. W.

**Ethylic Nitrosopropionate.** By G. LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], 11, 295—296; compare Abstr., 1894, i, 114).—An improved method of preparation. A mixture of alcoholic ethylic α-bromopropionate (100 grams in 300 grams of alcohol) and aqueous sodium nitrite (100 grams in 100 grams of water) is homogeneous. At the ordinary temperature, however, and in the course of 10 days, complete

interaction takes place, and, after the solvents have been allowed to evaporate from an open vessel in the cold, a large yield of crude ethylic nitrosopropionate (62 per cent.) may be extracted with ether from the residue; on recrystallisation from alcohol, the nitrosopropionate is obtained in long, light, brilliantly white needles. The method is applicable to the butyrates and valerate. J. N. W.

**Diamido-ethers.** By R. ANSCHÜTZ and K. STIEPEL (*Ber.*, 1895, **28**, 60—62).—Representatives of the class of diamido-ethers, of the general formula  $R \cdot C(NH_2)_2 \cdot OR'$ , have not hitherto been prepared.

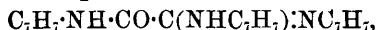
*Methylic dianilido-oxalate* (methylic dianilidomethoxyacetate),  $COOMe \cdot C(NHPh)_2 \cdot OMe$ , is obtained by acting with dry aniline on methylic dichloroxalate (methylic dichloromethoxyacetate),  $COOMe \cdot CCl_2 \cdot OMe$ , in dry ethereal solution. It is a viscid liquid, which decomposes when heated. It combines with 2 mols. of hydrogen chloride to form a solid *hydrochloride*, and it also yields a *platinochloride*.

*Methylic semiphenylimido-oxalate* (methylic phenylimidomethoxyacetate),  $COOMe \cdot C(OMe) \cdot NPh$ , is produced when the foregoing action is carried out in boiling xylene solution, and forms crystals melting at  $111^\circ$ . When ammonia is passed into an ethereal solution of this substance, *methylic amidoanilido-oxalate* (methylic amidoanilidomethoxyacetate),  $COOMe \cdot C(NH_2)(NHPh) \cdot OMe$ , is formed as a white powder which melts at  $215^\circ$ . The corresponding *diparatoluido*-compound melts at  $105^\circ$ , whilst the *dipiperido*-compound boils at  $166^\circ$  under a pressure of 20 mm. without undergoing decomposition.

*Methylic semiortho-oxamate*,  $CONH_2 \cdot C(OMe)_3$ , which melts at  $118^\circ$ , is obtained by heating methylic semiphenylimido-oxalate (methylic phenylimidomethoxyacetate) with ammonia dissolved in methylic alcohol.

Diphenylamidinoxalanilide,  $NHPh \cdot CO \cdot C(NHPh) \cdot NPh$ , which is found among the products of the action of aniline on methylic dichloroxalate (methylic dichloromethoxyacetate), has previously been described by Klinger (this Journ., 1877, i, 710), who gives the melting point as  $234\text{--}235^\circ$  instead of  $134\text{--}135^\circ$ .

*Diparatolylamidinoxaloparatoluidide*,



melts at  $182^\circ$ .

*Semiorthoaxalopiperidide*,  $NC_5H_{10} \cdot CO \cdot C(C_5NH_{10})_3 + 3MeOH$ , is a liquid, the constitution of which cannot as yet be regarded as proved. A. H.

**Glyoxylic acid.** By C. BOETTINGER (*Arch. Pharm.*, 1894, **232**, 549—557; compare Abstr., 1894, i, 402).—According to the author, glyoxylic acid cannot be crystallised, as the syrupy solution decomposes on further concentration; the minute bubbles of carbonic anhydride gave it, however, the appearance of a solid.

A gelatinous modification of the calcium salt is obtained by evaporating its solution and allowing it to cool. This jelly effloresces, especially in direct sunlight, and ultimately is suddenly transformed into a mixture of fine crystals and clear dilute solution.



The acid interacts with hydrazine sulphate to form an intensely red substance; in hot solutions, however, this is decomposed, and carbonic anhydride and ammonia are liberated. Ammonia decomposes glyoxylic acid in a similar manner.

A colourless, viscid liquid of spirituous odour, probably an *acetal*, results from the action of glyoxylic acid on alcohol in the presence of sulphuric acid in the cold, but is decomposed by heat into formaldehyde and other products. It is soluble in water, and forms a white, insoluble *calcium salt*.

A paste of glyoxylic acid and thiocarbamide acquires a bright scarlet colour, due to a substance containing sulphur and nitrogen. This is insoluble in alcohol, but freely soluble in alkalis forming a solution of the same colour, from which coloured compounds are precipitated by metallic salts. It cannot be obtained from formaldehyde or dichloroacetic acid; the latter forms a white product with thiocarbamide, which is only sparingly soluble in alkalis.

*Bisdimethylamidophenylacetic acid*,  $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{COOH}$ , crystallises in colourless needles from a solution of dimethylaniline and glyoxylic acid in the minimum quantity of alcohol. It melts at  $171^\circ$ , and is sparingly soluble in boiling water, readily in alkalis. The acid is dissolved by concentrated sulphuric and acetic acids. It is readily oxidised by air, mercuric chloride, &c., to a substance of intense blue colour, but is decomposed by bromine, parabromodimethylaniline being formed. The *ethylic salt* crystallises in slender, colourless needles, and melts at  $68^\circ$ .

$\alpha$ -Naphthylamine condenses with glyoxylic acid in alcoholic solution to form a bright brown powder,  $\text{C}_{12}\text{H}_9\text{NO}_2$ , which is soluble in ammonia, but insoluble in alcohol and dilute acids. The *barium salt* is reddish-brown.

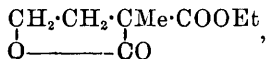
Similar products result from the condensation of orthotoluidine and metaphenylenediamine with glyoxylic acid; the first is intensely yellow, the second a black powder. Glyoxylic acid also condenses with resorcinol and catechol, but not with quinol or dimethoxyquinol, in the molecules of which the para-positions are occupied.

JX. W.

**Action of Ethylic Isosuccinate on Ethylenic Bromide. Constitution of Vinaconic acid.** By R. MARBURG (*Ber.*, 1895, 28, 8—12).—When ethylic sodioisosuccinate,  $\text{CMeNa}(\text{COOEt})_2$ , is treated in alcoholic solution with ethylenic bromide, about 15 per cent. of it is converted into *ethylic  $\gamma$ -bromethylisosuccinate*,

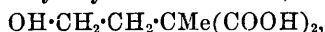


This is a colourless, rather viscous, oil, boiling at  $134$ — $135^\circ$  under 8 mm. pressure; at  $200^\circ$  it decomposes quantitatively into ethylic bromide and *ethylic  $\alpha$ -methylbutyrolactonecarboxylate*,



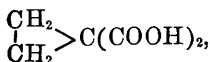
which boils at  $262$ — $263^\circ$  under 755 mm. pressure; the *acid* itself crystallises in colourless prisms and melts at  $98^\circ$ , it is obtained by

hydrolysing the bromo-acid with baryta water, and adding acid to the barium salt of  $\gamma$ -hydroxyethylis succinic acid,



formed; the acid is itself not capable of existence, but at once loses water and forms the lactone-acid.

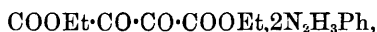
When, however, ethylic sodiomalonate, in which a hydrogen atom is still attached to the carbon atom, is treated with propylenic bromide, the ethylic salt of a bromo-acid is not formed, but instead the ethylic salt of a dibasic acid containing no bromine, *ethylic methylvinacconate* (*trimethylenedicarboxylate*), boiling at 106—107° under 8 mm. pressure. The action is not at all analogous to the preceding one, and hence there can be little doubt that vinaconic acid, which is formed in a similar way by the action of ethylenic bromide on ethylic sodiomalonate, is not vinylmalonic acid,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}(\text{COOH})_2$  (Fittig and Röeder, Abstr., 1883, 730), but trimethylenedicarboxylic acid,



(compare W. H. Perkin, jun., Trans., 1885, 801; 1887, 849).

C. F. B.

**Isomeric Osazones of Ethylic Dioxysuccinate.** By R. ANSCHÜTZ and H. PAULY (*Ber.*, 1895, 28, 64—69).—When ethylic dioxysuccinate is treated with phenylhydrazine a number of different compounds is formed. When the ethereal salt is added to an alcoholic solution of the hydrazine, an additive compound,



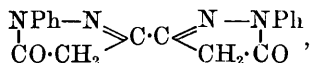
is obtained, which crystallises in fascicular groups of slender white needles, melting and decomposing at 116—118°. When this is kept, either alone or covered with ether, it is converted into the  $\alpha$ -osazone, whereas if covered with alcohol, it passes into the  $\beta$ -osazone. The *monophenylhydrazone* may be prepared by the addition of phenylhydrazine to a well cooled alcoholic solution of the ethereal salt. It melts at 72—73°, and when treated in ethereal solution with sulphurous anhydride or hydrogen chloride passes into a less soluble modification melting at 77°.

Three isomeric osazones have also been prepared, of which the  $\alpha$ -compound has already been described (Abstr., 1891, 725). The three differ from one another in crystalline habit, melting point, and solubility. The  $\alpha$ -compound melts at 120—121°, the  $\beta$ -compound at 136—137°, and the  $\gamma$ -compound at 173—175°; the  $\beta$ - and  $\gamma$ -compounds are respectively 10 and 100 times less soluble in ether than the  $\alpha$ -compound. The  $\alpha$ -modification readily changes into the  $\beta$ -form when iodine or sulphurous anhydride is added to its ethereal solution. Both the  $\alpha$ - and  $\gamma$ -forms are changed into the  $\beta$ -form when they are boiled for some time with an indifferent solvent. It has hitherto been found impossible to convert the  $\beta$ -form into either of the others. All three modifications are converted by acetic acid into the same pyrazolone-derivative as was obtained from the  $\alpha$ -modification by Anschütz and Parlato (Abstr., 1892, 1181). The  $\alpha$ -osazone is converted by

oxidation into the corresponding *osotetrazone*,  $\text{NPh}\cdot\text{N}:\text{C}(\text{COOEt})_2$ , which crystallises in slender, violet-black needles, or flat, garnet-red prisms, melting and decomposing at  $143^\circ$ . The  $\beta$ - and  $\gamma$ -modifications do not yield this substance. Propylic dioxysuccinate behaves towards phenylhydrazine in a similar manner to the ethylic salt. An additive compound, melting at  $112^\circ$ , is the first product, and isomeric osazones have been obtained but not yet investigated. They are converted by acetic acid into a pyrazolone derivative melting at  $115^\circ$ .

With phenylhydrazine, the pyrazolone-compounds obtained by heating the osazones of both the propylic and ethylic salts yield a compound, which melts at  $256^\circ$ ; its formula is  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_3$ , but its constitution has not yet been ascertained.

The osazone of ethylic ketipate is also converted by acetic acid into a substance which melts and decomposes at  $275^\circ$  and seems to be a bis-pyrazolone derivative of the formula



although it may possibly be a bis-pyridazolone-compound.

A. H.

**Disubstituted Alkylic Tartrates.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1894, [3], 11, 305—317).—In order to test the validity of Guye's well-known formula, the rotatory powers of the alkylic salts of various acidyltartrac acids of the type of methylic diacetyltartrate were determined. As these were mostly liquids of uncertain stability at their boiling points, the mode of purification of the product obtained by the action of the alkylic tartrate on the acid chloride at  $100^\circ$  was modified, the ethereal salt being extracted from the washed product with ether, and the latter removed from the dried extract in a dry atmosphere and at a low temperature.

The alkylic diacidyltartrates are heavy, tasteless, neutral solids or liquids, which decompose readily when distilled, even under very low pressures. The boiling points rise, and the densities diminish, as the series is ascended. Cryoscopic observations in benzene and ethylenic bromide show that the molecules are simple. The rotatory powers, whether of the liquids or of their alcoholic solutions, are practically independent of the temperature. The diacidyltartrates are completely hydrolysed by alkalis or sodium ethoxide, and partially and slowly by water; they are resolved by alcoholic ammonia, at a high temperature, into the alcohols, the fatty amides, and tartramide, the latter undergoing further hydrolysis into tartramic acid. They are decomposed by phosphoric pentachloride into the fatty acid chlorides, and the alkylic chlorotartrates, but the latter decompose further, especially at high temperatures, into hydrogen chloride and the corresponding chlorofumarates.

*Methylic diacetyltartrate* crystallises in rhomboidal, oblique prisms, melts at  $103^\circ$ , and boils at  $182$ — $183^\circ$  (21 mm.). The rotatory power in alcoholic solution is  $[\alpha]_D = -15.5^\circ$ . The *ethylic* salt crystallises in clinorhombic prisms, melts at  $66.5^\circ$ , and boils at  $190$ — $192^\circ$ .

(21 mm.), and at 291° under atmospheric pressure. The rotatory power of the superfused substance is  $\alpha = +5^\circ$  for 100 mm.; of the alcoholic solution,  $[\alpha]_D = +0.3^\circ$ . The *propylic* salt melts at 31°, and boils at 195–197° (13 mm.), at 204° (16 mm.), at 216° (70 mm.), at 233–235° (100 mm.), and at 313° under atmospheric pressure. The rotatory power of the superfused substance is  $\alpha = 13.4^\circ$  for 100 mm.; of the alcoholic solution,  $[\alpha]_D = +7.0^\circ$ . *Butylic tartrate* crystallises in elongated prisms, melts at 21–22°, and boils at 208° (12 mm.); sp. gr. = 1.098 at 22°. The rotatory power of the superfused substance is  $[\alpha]_D = +10.3^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +11.3^\circ$ . *Butylic diacetyltartrate* boils at 214° (20 mm.), and at 218° (23 mm.); sp. gr. = 1.096 at 15.5°. The rotatory power of the liquid at 20°,  $[\alpha]_D = +8.0^\circ$ ; of the alcoholic solution at 22°,  $[\alpha]_D = +8.8^\circ$ .

*Methylic dipropionyltartrate* crystallises in large prisms. It melts at 27–27.5°, and boils at 184–185° (12 mm.), at 189–190° (15 mm.), and at 287–289° (730 mm.); sp. gr. = 1.181 at 15°. The rotatory power of the superfused substance at 15°,  $[\alpha]_D = -10.7^\circ$ ; of the alcoholic solution at 20°,  $[\alpha]_D = -12.4^\circ$ . The *ethylic* salt boils at 202° (16 mm.), and can be distilled, with but little decomposition, under atmospheric pressure; sp. gr. = 1.124 at 14°. The rotatory power of the liquid at 23°,  $[\alpha]_D = +0.4^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +1.2^\circ$ . The *propylic* salt boils at 207° (15 mm.), and at 222–225° (45 mm.); sp. gr. = 1.018 at 15°. The rotatory power of the liquid at 16°,  $[\alpha]_D = +5.6^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +6.3^\circ$ . The *butylic* salt boils at 212° (12 mm.), at 216° (20 mm.), and at 230–231° (36 mm.); sp. gr. = 1.068 at 15.5°. The rotatory power of the liquid at 12°,  $[\alpha]_D = +6.9^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +8.0^\circ$ .

*Methylic dibutyryltartrate* boils at 200–203° (11 mm.), at 212° (26 mm.), and at 300–302° (731 mm.); sp. gr. = 1.145 at 14°. The rotatory power of the liquid at 13°,  $[\alpha]_D = -15.1^\circ$ ; of the alcoholic solution,  $[\alpha]_D = -12.6^\circ$ . The *ethylic* salt boils at 212–215° (24 mm.); sp. gr. = 1.105 at 15.5°. The rotatory power of the liquid at 16°,  $[\alpha]_D = -0.8^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +0.3^\circ$ . The *propylic* salt boils at 208–211° (17 mm.), at 221–222° (28 mm.), and at 226–227° (40 mm.); sp. gr. = 1.067 at 15.5°. The rotatory power of the liquid at 13°,  $[\alpha]_D = +5.2^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +7.2^\circ$ .

The divaleryl tartrates were prepared by means of *normal valeric chloride*. This is a liquid which boils at 127–128°, and has sp. gr. = 1.0155 at 15°. *Methylic divaleryl tartrate* boils at 208–210° (11 mm.); sp. gr. = 1.101 at 18°. The rotatory power of the liquid at 15°,  $[\alpha]_D = -16.1^\circ$ ; of the alcoholic solution,  $[\alpha]_D = -12.9^\circ$ . The *ethylic* salt boils at 214–215° (11 mm.); sp. gr. = 1.068 at 12°. The rotatory power of the liquid at 15°,  $[\alpha]_D = 2.0^\circ$ ; of the alcoholic solution,  $[\alpha]_D = -0.7^\circ$ . The *propylic* salt boils at 223° (12 mm.); sp. gr. = 1.050 at 16.5°. The rotatory power of the liquid at 17°,  $[\alpha]_D = +3.3^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +3.6^\circ$ . The *butylic* salt boils at 229–230° (13 mm.), at 243° (28 mm.), at 269–270° (60 mm.), and at 340–350° under atmospheric pressure; sp. gr. = 1.031 at 13°. The rotatory power of the liquid at 15°,  $[\alpha]_D = +4.8^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +6.0^\circ$ .

*Methylic dicaproyltartrate* has a sp. gr. = 1.078 at 14°. The rotatory power of the liquid at 16° is  $[\alpha]_D = -15.9^\circ$ ; of the alcoholic solution,  $[\alpha]_D = -12.4^\circ$ . The *ethylic* salt has a sp. gr. = 1.049 at 14.5°. The rotatory power of the liquid at 16° is  $[\alpha]_D = +3.1^\circ$ ; of the alcoholic solution,  $[\alpha]_D = +1.1^\circ$ . The *propylic* salt boils at 242—243° (40 mm.); sp. gr. = 1.027 at 15°. The rotatory power of the liquid at 16°,  $[\alpha]_D = -2.2^\circ$ ; of the alcoholic solution,  $[\alpha]_D = -3.6^\circ$ .

The rotatory powers of these alkylic acidyltartrates vary in general in the same sense as Guye's product of asymmetry, the introduction of positive radicles causing a positive increase or negative decrease in both, and that of negative radicles having the opposite effect. But there are certain modifications necessary, for the addition of a  $-\text{CH}_2$  group has a greater effect when the radicle is alkylic than when it is oxylic, so that the structure of the latter kind must be closer, or more compressed, than that of the former. To allow for the corresponding difference in the moments of the masses of the radicles, the author introduces a fifth quantity,  $m$ , into Guye's formula; a multiple of the mass of a  $-\text{CH}_2$  group. The formula thus becomes

$$P = \frac{m(a - c)(a - d)(a - c - m)(a - d - m)(c - d)}{(2a + b + c + d - m)^6}.$$

The influence of  $m$  increases with the length of the chain, but is not always exerted in the same sense, so that the value of  $P$  passes in any particular series through several maxima and minima. A corresponding change in sign is to be expected in the rotatory power, and may be observed in several instances; between methylic tartrate and methylic diacetyltartrate, for instance, also in the ethylic series, and in the dibutyryltartrates.

		P.	$[\alpha]_D$ .
Methylic dibutyryltartrate	.....	-19.35	-15.1°
Ethylic	.....	-9.23	-0.8
Propylic	.....	0	+6.2
Butylic	.....	+7.0	+6.0

The modified form of Guye's formula is therefore valid qualitatively, even when the substituted chains are of considerable length.

JN. W.

**Sarcosine.** By W. PAULMANN (*Arch. Pharm.*, 1894, **232**, 601—639).—Sarcosine is best prepared by the hydrolysis of caffeine with baryta, the yield being 60 per cent. of the theoretical; the yield obtained by the action of ethylic chloracetate on methylamine is extremely poor. The free base is conveniently prepared from the hydrochloride by neutralising it with an alkali, and extracting the evaporated residue with alcohol. The *hydrobromide*, *hydriodide*, and other salts are described. There does not seem to be an oxalate, so that the basic properties of sarcosine are less marked than those of glycocine; the same is true of the acid properties, for neither the alkali nor silver salts, nor those of the alkaline earths, nor the alkylic salts could be prepared; the *nickel* and *zinc* salts are described. In preparing

betaine by the action of methylic iodide on sarcosine, the methylic compound of the latter was obtained; its *platinochloride* is described. The formation of dimethylamine (Abstr., 1884, 994) in the dry distillation of sarcosine, as described by Mylius, was not observed. Nitrososarcosine possesses acid properties stronger than those of the parent substance, as it forms calcium and *silver* as well as *copper* and *nickel* salts; a barium salt, however, could not be prepared; the basic properties are very feeble, as it does not form a *platinochloride* or an *aurochloride*. On reducing an acetic acid solution of the calcium salt with zinc dust, a substance having strongly reducing properties is formed.

Sarcosine hydrochloride is converted by a mixture of fuming nitric and fuming sulphuric acids into *nitrosarcosine*,  $\text{NO}_2\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{COOH}$ , a yellow, crystalline, hygroscopic powder, melting at  $164\text{--}168^\circ$ . This gives the nitrate reaction with ferrous sulphate and sulphuric acid, and a colour-reaction with sulphuric acid and phenol resembling that given by guanidine.

*Benzoylsarcosine* (methylhippuric acid),  $\text{NMeBz}\cdot\text{CH}\cdot\text{COOH}$ , could not be crystallised, owing to its extreme solubility; the *calcium* and *copper* salts are described. *Acetylsarcosine* (methylaceturic acid) crystallises in long, thick needles, and melts at  $134\text{--}138^\circ$ ; the *copper* and *silver* salts are described. JN. W.

**Paradimethylamidobenzyllic Alcohol.** By L. ROUSSET (*Bull. Soc. Chim.*, 1894, [3], 11, 318—320).—This alcohol was prepared from paradimethylbenzaldehyde, made by projecting the condensation product of dimethylaniline and chloral hydrate in small portions at a time into boiling 30 per cent. caustic soda (compare Knoefler and Boessneck, Abstr., 1888, 267). The aldehyde, which crystallises out on cooling, is pure enough for most experiments; on reduction with sodium amalgam in aqueous alcoholic solution, it does not yield the expected alcohol, but a *substance* melting at  $155^\circ$ , which is under investigation. The alcohol is best prepared by the action of boiling, concentrated, aqueous potash; the portion of the product insoluble in water, but soluble in ether, consists chiefly of the alcohol, whilst the soluble portion consists of the potassium salt of *paradimethylamidobenzoic acid*; this acid melts at  $235^\circ$ . The ethereal solution on fractionation under low pressure yields *paradimethylamidobenzyllic alcohol*, which forms white crystals, melts at  $62^\circ$ , and boils at  $180\text{--}190^\circ$  (18 mm.); it is turned yellow by light. The *platinochloride* crystallises in yellow needles. The *acetate* forms reddish-white crystals and melts at  $102^\circ$

JN. W.

**Action of Phosphorus Pentachloride on Succinil.** By R. ANSCHÜTZ and C. BEAVIS (*Ber.*, 1895, 28, 57—58; compare Abstr., 1891, 1047).—In addition to dichloromaleinanil dichloride, described in their previous paper, the authors have obtained *tetrachloro-1-phenylpyrroline*,  $\text{C}_6\text{H}_5\text{NCl}_4\text{Ph}$ , by the action of phosphorus pentachloride on succinil. This compound melts at  $93^\circ$ , and is less soluble in light petroleum than the dichloromaleinanil chloride.

Dichloromaleinanil itself, when treated with phosphorus pentachlo-

ride, yields *tetrachlorosuccinanil*,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CCl}_2 \\ | \\ \text{CO} \cdot \text{CCl}_2 \end{smallmatrix}$ , melting at  $157^\circ$ , and also dichloromaleïnänil chloride.

Dichloromaleïnänil reacts with bases when heated with them. Aniline produces *anilidochloromaleïnänil*,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{NHPh} \\ | \\ \text{CO} \cdot \text{CCl} \end{smallmatrix}$ , melting at  $188^\circ$ , whilst monomethylaniline yields the corresponding *methyl-derivative*, melting at  $189^\circ$ .

Dichloromaleïnänil dichloride also reacts with aniline, *dichloromaleïndianil*,  $\text{CCl} \begin{smallmatrix} \text{CCl} \cdot \text{C} \cdot \text{NPh} \\ | \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$ , which melts at  $186^\circ$ , being formed.

*Dichloromaleïn-paratoluidipiperidide*,  $\text{CCl} \begin{smallmatrix} \text{CCl} \cdot \text{C} \cdot (\text{C}_5\text{NH}_{10})_2 \\ | \\ \text{CO} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Me} \end{smallmatrix}$ , separates from acetone in splendid yellow crystals, and melts at  $107^\circ$ . On reduction, dichloromaleïnänil dichloride is converted into  $\gamma$ -*anilidobutyrolactam*,  $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$ , which melts at  $68^\circ$ .

A more detailed account of these investigations is shortly to be published. A. H.

**Constitution of Succinanil.** By R. ANSCHÜTZ (*Ber.*, 1895, 28, 59—60; compare the foregoing Abstr.).—The formation of tetrachloro-1-phenylpyrroline from succinanil is a strong argument in favour of the symmetrical formula,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$ , for the latter substance. The reduction of dichloromaleïnänil dichloride to  $\gamma$ -anilidobutyrolactam also seems to show that dichloromaleïnänil, and therefore also succinanil, are symmetrical. There is thus not a single fact in favour of the asymmetrical formula. A. H.

**Paramidoacetophenone and Paramidophenylmethylcarbinol.** By L. ROUSSET (*Bull. Soc. Chim.*, 1894, [3], 11, 320—322).—Paramidoacetophenone is best prepared by heating acetanilide, acetic anhydride, and zinc chloride in molecular proportions in a reflux apparatus on an oil bath for several hours; the oily product is then poured into water, partially neutralised with caustic soda, and the pasty mass which separates on cooling is dissolved in concentrated hydrochloric acid. The liquid thus obtained is made alkaline with soda, and the aniline, liberated from the unchanged acetanilide, is distilled off with steam; the paramidoacetophenone is separated from the residue partly in the crystalline form, and partly by extraction with ether and alcohol. The purified ethereal solution on fractionation yields the ketone, boiling at  $195$ — $210^\circ$  under 18 mm. pressure, and in quantity amounting to 26 to 30 per cent. of the acetanilide employed (compare Drewsen, Abstr., 1882, 847, and Klinger, Abstr., 1886, 60). Paramidoacetophenone, when reduced with sodium amalgam in aqueous alcoholic solution, yields a substance crystallising in white needles and melting at  $250^\circ$ , and an oil which, on purification, yields *paramidophenylmethylcarbinol*; the latter forms white crystals, is

soluble in water and in the usual solvents, and turns yellow on exposure to light. It melts at  $93^{\circ}$ , and boils under 18 mm. pressure at  $190^{\circ}$ . The *platinochloride* crystallises in small, yellow needles. The diacetyl-derivative,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OAc}$ , forms white crystals and melts at  $192^{\circ}$ .  
J. N. W.

**Diagnosis of Orthosubstituted Aromatic Acids by means of the Iodoso-reaction.** By V. MEYER (*Ber.*, 1895, 28, 83—84).—It has been shown by the author and his students that orthoiodobenzoic acids are converted into iodoso-derivatives (1) by solution in fuming nitric acid; (2) by boiling with potassium permanganate and sulphuric acid; (3) by the action of an alkali on the iododichlorides. The meta- and para-iodo-acids are nitrated by the first method, not altered or completely oxidised by the second, and regenerate the iodides from the iododichlorides. Willgerodt's preparation of meta- and para-iodoso-acids (*Abstr.*, 1894, i, 590) by other methods in no way invalidates the author's statement that the above reactions afford a ready means of distinguishing orthoiodo-acids from the para- and meta-compounds. The paper concludes with a summary of Grahl's investigation of iodo-isophthalic acid.  
J. B. T.

**Electrolytic Reduction of Paranitrobenzoic acid.** By A. A. NOYES and A. A. CLEMENT (*Amer. Chem. J.*, 1894, 16, 511—513; compare *Abstr.*, 1893, i, 406).—The authors have previously shown that paramidophenolorthosulphonic acid is obtained on electrolysing nitrobenzene in sulphuric acid solution. This behaviour is characteristic of nitro-compounds in general (compare Gattermann, *Abstr.*, 1894, i, 72), the reduction of the nitro-group being accompanied by a migration of one of its oxygen atoms to the para-position. Only those compounds in which the para-position is already occupied by some group or element other than hydrogen form exceptions to this rule. Paranitro-orthotoluidine, for example, gives rise to diamidocresol,  $[\text{Me} : (\text{NH}_2)_2 : \text{OH} = 1 : 2 : 4 : 5]$ , a migration of oxygen to the ortho-position taking place. Paranitrotoluene similarly yields amidobenzylic alcohol, a substitution of hydroxyl in the methyl group occupying the para-position. On electrolysis of a warm solution of paranitrobenzoic acid (12 grams) in concentrated sulphuric acid (100 grams), by passing a current of 1 ampère for 24 hours, paramidophenolsulphonic acid is formed, the tendency of the oxygen atom to assume the para-position having been sufficient to expel the carboxyl-group originally occupying it.  
G. T. M.

**Preparation of Benzoic Anhydride.** By A. DENINGER (*J. pr. Chem.*, 1894, [2], 50, 479—480).—Although benzoic chloride does not react with dry sodium carbonate, a violent action takes place when pyridine is added to the mixture, the anhydride being formed quantitatively. Picoline or quinoline may be substituted for pyridine, but dimethylaniline does not produce the same effect.

Mercuric oxide, cupric oxide, and litharge all behave in a similar manner to sodium carbonate; zinc oxide acts without the addition of pyridine, whilst barium carbonate and ferric oxide do not produce



the violent action under any circumstances (compare Claisen, this vol., i, 139).  
A. H.

**Bismuth Nitrosalicylates.** By H. CAUSSE (*Compt. rend.*, 1894, 119, 690—699).—Double decomposition between bismuth nitrate and a soluble salicylate is rarely complete, and a reaction gradually takes place in the mother liquor, the result depending on the concentration. Sometimes white, silky needles separate; sometimes the colour of the crystalline precipitate is yellow or orange. Even in dilute solutions, the nitric acid of the bismuth nitrate converts the salicylic acid into  $\beta$ -nitrosalicylic acid, which yields normal and basic salts according to the conditions, the energy of the phenolic function being augmented by the introduction of the  $\text{NO}_2$  group. The red colour of bismuth salicylate, which is usually attributed to iron, is really due to a nitrosalicylate. *Bismuth  $\beta$ -nitrosalicylate*,  $[\text{C}_6\text{H}_3(\text{NO}_2)(\text{OH})\cdot\text{COO}]_3\text{Bi} + 2\text{H}_2\text{O}$ , is obtained in long, silky needles from the mother liquor from the preparation of bismuth salicylate, and also by dissolving 20 grams of salicylic acid in 100 c.c. of acetic acid and adding 150 c.c. of water and 15 grams of normal bismuth nitrate dissolved in 50 c.c. of a saturated solution of potassium nitrate; an action at once begins, and soon becomes violent if the liquid is not cooled. The nitrosalicylate is decomposed by boiling water into bismuth oxide and nitrosalicylic acid; with ferric chloride it gives an intense red coloration.

*Basic bismuth  $\beta$ -nitrosalicylate*,  $\text{OH}\cdot\text{Bi} < \begin{smallmatrix} \text{COO} \\ \text{---O---} \end{smallmatrix} > \text{C}_6\text{H}_3\text{NO}_2 + \text{H}_2\text{O}$ , is obtained by gently heating a solution of 20 grams of salicylic acid in 100 c.c. of acetic acid with a solution of 30 grams of bismuth nitrate in 300 c.c. of a saturated solution of potassium nitrate. The salt forms small, lemon-yellow needles, with properties similar to those of the normal salt; it is decomposed by water, and gives a red coloration with ferric chloride. A second *basic bismuth nitrosalicylate*,  $\text{Bi}_2(\text{OH})_2[\text{C}_6\text{H}_3(\text{NO}_2)(\text{OH})\cdot\text{COO}]_2 + \text{H}_2\text{O}$ , separates in orange-red, microscopic needles when the liquid from which the preceding compound has separated is very nearly neutralised with sodium carbonate.

*$\beta$ -Nitrosalicylic acid*,  $[\text{COOH}:\text{OH}:\text{NO}_2 = 1:2:5]$ , is obtained by the action of boiling water on any one of the bismuth nitrosalicylates. It crystallises from water and melts at  $227.5^\circ$ . It gives a blood-red coloration with ferric chloride, and forms a barium salt which crystallises in lemon-yellow lamellæ.  
C. H. B.

**Synthesis of  $\alpha$ -Phenyl- $\beta$ -benzoylpropionic acid.** By R. ANSCHÜTZ and W. MONTFORT (*Ber.*, 1895, 28, 63—64).—In order to confirm a previously expressed view as to the formation of mesitonic acid from mesityl oxide (*Abstr.*, 1888, 1272), the authors have effected the synthesis of  $\alpha$ -phenyl- $\beta$ -benzoylpropionic acid from benzylideneacetophenone. The additive compound of this ketone with hydrogen chloride,  $\text{CHPhCl}\cdot\text{CH}_2\cdot\text{COPh}$  (Claisen and Claparède, *Abstr.*, 1882, 511), can readily be converted into the *nitrile* which melts at  $127^\circ$ , and the *acid* melting at  $153^\circ$ .  $\alpha$ -Phenyl- $\beta$ -benzoylpropionic acid is converted by reduction into  $\alpha$ - $\gamma$ -diphenylbutyrolactone,  
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$\text{CHPh} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CHPh} \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , which melts at  $109^\circ$ . Acetic chloride converts the acid into  $\alpha$ - $\gamma$ -diphenylcrotonolactone,  $\text{CHPh} < \begin{smallmatrix} \text{CH} \cdot \text{CHPh} \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , which melts at  $103^\circ$ . The phenylhydrazone is unstable and is readily converted into triphenylpyridazolone,  $\text{N} < \begin{smallmatrix} \text{CPh} \cdot \text{CH}_2 \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} > \text{CHPh}$ . Full details of the investigation are to be shortly published. A. H.

**Ethylic Dinitrotterephthalate: A Correction.** By C. HAEUSER-MANN and E. MARTZ (*Ber.*, 1895, 28, 81—82).—By the action of alcohol and hydrogen chloride on dinitrotterephthalic acid,  $[(\text{NO}_2)_2 = 3 : 5]$ , the ethylic hydrogen salt is formed, not the diethylic salt as previously stated (*Abstr.*, 1894, i., 131). The acid therefore follows V. Meyer's rule. The ethylic hydrogen salt readily dissolves in alkalis, is not reddened by excess, and on warming in aqueous solution, decomposes silver carbonate, a soluble silver salt being produced. J. B. T.

**Derivatives of Gallic acid.** By C. BOETTINGER (*Arch. Pharm.*, 1894, 232, 545—549, compare *Abstr.*, 1892, 181, and 1894, i, 13).—The action of a mixture of glycerol and hydrogen potassium sulphate on gallic acid is not analogous to its action on tannin, as, instead of condensation and hydration, reduction and oxidation take place; a similar action occurs in the reduction of dialuric acid to acid ammonium hydrurate by this mixture.

The products are separated by means of alcohol; the relative yield varying accordingly as the gallic acid is hydrated or anhydrous. The reduction product, *hydrogallic acid*,  $\text{C}_{14}\text{H}_{16}\text{O}_8 + \text{H}_2\text{O}$ , has the same formula as octohydroxygallic acid, and is peach coloured. It is insoluble in water, but soluble in alcohol, methylic alcohol, aniline, and ammonia; the colour of the ammoniacal solution is at first blue, but soon changes through intense violet to brown. Hydrogallic acid is almost entirely destroyed by fusion with potash, and yields only a small quantity of a very oxidisable oil, when distilled with zinc dust; this oil does not possess the characteristic odour of the corresponding products from hydrotannic and hydroquercitannic acids. The acid dissolves freely in fuming sulphuric acid. The *acetyl* derivative,  $\text{C}_{14}\text{H}_{14}\text{Ac}_2\text{O}_8$ , crystallises in yellowish-grey plates.

The oxidation product,  $\text{C}_{12}\text{H}_{14}\text{O}_9 + 2\text{H}_2\text{O}$ , appears to be a derivative of pyrogallol; it is a dull, brownish-violet powder, and is insoluble in water and ammonia, although its colour is changed to violet by the latter. It yields an *acetyl* derivative,  $\text{C}_{12}\text{H}_{13}\text{AcO}_9$ , a brownish-grey substance insoluble in water, alcohol, and cold dilute soda.

JN. W.

**Stereoisomerism of Diazo-Compounds.** By A. HANTZSCH (*Ber.*, 1894, 27, 3527—3547; compare E. Bamberger, this vol., i, 25).—The unstable character of potassium benzenesyndiazosulphonate renders the analyses of little value in determining its composition;

salts of analogous diazo-compounds, however, may be analysed without difficulty, owing to their greater stability.

*Potassium parachlorobenzenesyndiazosulphonate*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N} \begin{smallmatrix} \parallel \\ \text{N} \end{smallmatrix} \text{SO}_3\text{K} + \text{H}_2\text{O}$ , is obtained in bright red crystals which remain unchanged in air for several hours, but ultimately become discoloured; the *anti*-salt is anhydrous.

*Potassium parabromobenzenesyndiazosulphonate* also contains  $1\text{H}_2\text{O}$ , and becomes discoloured on exposure to air. *Potassium orthochlorobenzenesyndiazosulphonate* is anhydrous. It is deep red, and more soluble than the para-derivative, being also the most stable of these salts; the *anti*-compound forms yellow needles.

The degree of purity of a preparation of potassium benzenesyndiazosulphonate is indicated by titration with iodine solution, this process yielding good results when performed rapidly; the halogenised *syn*-salts, although more stable, are less soluble in water, and the results are not therefore so satisfactory, in consequence of polymerisation taking place.

The author points out the analogy existing between the potassium salt of mercury sulphonic acid,  $\text{Hg}(\text{SO}_3\text{K})_2$ , and the stereoisomeric diazo-salts. Cryoscopic determinations indicate that both the latter are resolved on solution into the ions  $\text{PhN}:\text{N}\cdot\text{SO}_3$  and  $\text{K}$ ; they are, therefore, structurally identical, because a salt having the form of a true sulphite would dissociate into the ions  $\text{PhN}:\text{N}$ ,  $\text{SO}_3$ , and  $\text{K}$ . Moreover, under this condition, the solutions would be colourless, which is not the case with the salts in question.

On these additional grounds, the author adheres to the conclusion that the isomerism exhibited by the two potassium benzenediazosulphonates is geometrical in character. M. O. F.

**Parachlorometasulphobenzoic acid and its Derivatives.** By H. M. ULLMANN (*Amer. Chem. J.*, 1894, **16**, 530—543).—This acid is best prepared by distilling sulphuric anhydride from fuming sulphuric acid directly into a receiver containing the dried powdered parachlorobenzoic acid; the mixture is heated occasionally for some hours, the excess of sulphuric anhydride is distilled off, and the product converted into the barium salt. On adding an equivalent quantity of sulphuric acid to this, the free acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COOH} + 3\text{H}_2\text{O}$ , is obtained; it crystallises from water in long needles, and forms a dimorphous barium salt, both varieties of which contain  $3\text{H}_2\text{O}$ . On heating the acid with phosphorous pentachloride and ammonia successively, a product was obtained which proved not to be parachlorobenzoic sulphinide (compare Roode, *Abstr.*, 1891, 1226), but a diamide. The sulphonic and carboxyl groups must therefore be in the meta-position, the acid having the constitution  $[\text{COOH}:\text{SO}_3\text{H}:\text{Cl} = 1:3:4]$ . The normal sodium salt, on treatment with two equivalents of phosphorous pentachloride, gives rise to the *dichloride*,  $\text{SO}_2\text{Cl}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COCl}$ , which crystallises from light petroleum in flakes, and from ether in needles, and melts at  $42\text{--}43^\circ$ , and a *monochloride*,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COCl}$ , which is insoluble in cold, light petroleum, crys-

tallises from ether in needles, and melts at 163—167°. The *disulphonamide*,  $\text{SO}_2\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CONH}_2$ , corresponding with the dichloride, crystallises from hot water in needles, and melts at 233°; the *dianilide* melts at 219—220°. G. T. M.

**Illicene.** By A. SCHEEGANS and E. BRONNERT (*Arch. Pharm.*, 1884, **232**, 532—539).—*Illicene*,  $\text{C}_{36}\text{H}_{60}$ , is a hydrocarbon obtained from the bark, wood and leaves of the common holly (*Ilex aquifolium*, Linn.); it crystallises from alcohol in silky bunches of thin, colourless needles, and melts at 182—183°; when distilled, even under diminished pressure, it decomposes. It is freely soluble in the usual organic solvents, but less soluble in cold glacial acetic acid and light petroleum, and insoluble in water. The molecular weight was determined by cryoscopic observations on the benzene solution. It appears to contain a methylene group, as the substance condenses with acid anhydrides to form acidyl derivatives. These crystallise in colourless needles or plates: *diacetylillicene* melts at 219·5°; *dipropionylillicene* at 209°; *dibenzoylillicene* at 188°. With hydrogen chloride and concentrated sulphuric acid, illicene yields only resinous products, and it does not appear to form a picric acid derivative. On bromination, it yields a crystalline derivative of lower melting point; and on oxidation a mixture of acid and neutral substances.

Illicene is undoubtedly identical with a substance isolated by Personne from bird-lime made from the inner bark of the holly, but which he erroneously described as an alcohol, illicic alcohol,  $\text{C}_{25}\text{H}_{44}\text{O}$  (*Abstr.*, 1884, 1365). JN. W.

**Action of Acid Chlorides on Sodium Paranitrophenylnitrosamine.** By O. KÜHLING (*Ber.*, 1895, **28**, 41—43).—Paranitrodiphenyl (m. p. 113—114°) is formed when an acid chloride acts on sodium paranitrophenylnitrosamine suspended in dry benzene. Employing toluene in place of benzene, 4:4'-*methylnitrodiphenyl* is obtained; this crystallises in yellowish-white prisms, and melts at 103—104°. M. O. F.

**Constitution of Fluorescein.** By C. GRAEBE (*Ber.*, 1895, **28**, 28—31).—Resorcinolphthalein is formed on heating fluorescein with fused caustic potash, and the diethylic ether, which melts at 175—176°, is obtained from phthalic anhydride and resorcinol diethylic ether; it is clearly, therefore, a derivative of orthobenzoylbenzoic acid, and from the fact that no anthraquinone-derivative is obtained on treating resorcinolphthalein or its ethers with dehydrating agents, it seems probable that the carbonyl group is situated between two hydroxyl groups.

On these grounds, the author represents the constitution of fluorescein by the formula,  $\text{CO} < \text{C}_6\text{H}_4 > \overset{1}{\text{C}} < \text{C}_6\text{H}_3(\text{OH}) > \overset{6}{\text{O}}$ , pointing out, in support of this view, that the phthalins obtained from fluorescein and fluorescein chloride do not yield anthracene derivatives under the influence of concentrated sulphuric acid. The author attributes the

colour of fluoresceïn to its relationship with fluoran, which, although colourless, might be expected to yield coloured hydroxy-derivatives.

M. O. F.

**Constitution of Fluoresceïn.** By R. NIETZKI and P. SCHRÖTER (*Ber.*, 1895, **28**, 44—56).—When the alkaline solution of fluoresceïn ethylic ether (Herzig, *Abstr.*, 1892, 1319) is oxidised with potassium ferricyanide and acidified with glacial acetic acid, the *ethylic salt* of fluoresceïn,  $C_{22}H_{16}O_5$ , is obtained as a yellowish-brown precipitate. It separates from dilute alcohol or from glacial acetic acid in large crystals with a green lustre, and melts at  $247^\circ$ ; the solution in caustic alkalis or alkali carbonates yields fluoresceïn when boiled. Bromine converts it into erythrin.

On heating the ethylic salt of fluoresceïn in alcoholic solution with sodium ethoxide (1 mol.) and excess of ethylic bromide, for some hours at  $100^\circ$ , the *ethylic ether*,  $C_{24}H_{20}O_5$ , is obtained; it crystallises from alcohol in dark yellow needles, which become orange-red when dried at  $120$ — $130^\circ$ , and melt at  $159^\circ$ . Bromo-derivatives are obtained with difficulty; they are yellow dyes. This ether is identical with Baeyer's monethylic ether (*Annalen*, 1876, **183**, 1), which becomes colourless when recrystallised several times.

*Fluoresceïn ethylic ether*,  $C_{22}H_{16}O_5$ , obtained from the foregoing compound by the action of alcoholic potash, crystallises from dilute alcohol in yellow, rhombic plates which melt at  $251^\circ$ . Its solution in alkalis exhibits a green fluorescence which is less intense than that of fluoresceïn. The *bromo-derivative* is almost colourless, resembling Baeyer's eosin ethylic ether in this respect. The *acetyl derivative* melts at  $222^\circ$ .

The action of ethylic bromide on potassium fluoresceïn gives rise to the three ethers already described together with a colourless diethylic ether, which crystallises in long needles and melts at  $183^\circ$ . It is identical with Baeyer's diethylic ether (*loc. cit.*), and with the isofluoresceïn diethylic ether of O. Fischer and E. Hepp (this vol., i, 55). On reduction, it yields fluoresceïn diethylic ether which melts at  $187^\circ$ .

*Fluoresceïn triethylic ether*,  $C_{26}H_{26}O_5$ , is obtained by heating Herzig's diethylic ether (*loc. cit.*) with sodium ethoxide and ethylic bromide for some hours at  $100^\circ$ . It crystallises in colourless needles which melt at  $110^\circ$ , and when it is boiled with alcoholic potash the diethylic ether is regenerated.

The theoretical bearing of these results is then considered.

M. O. F.

**Phthaleïns of Orthosulphoparatoluic acid.** By J. A. LYMAN (*Amer. Chem. J.*, 1894, **16**, 513—528).—*Phenylparamethylsulphophthaleïn*,  $\begin{matrix} C_6H_3Me \\ | \\ SO_2-O \end{matrix} > C(C_6H_4.OH)_2$ , is obtained on gradually heating a mixture of carefully dehydrated orthosulphoparatoluic acid (1 mol.) and crystallised phenol (2 mols.) to  $170^\circ$ . It is a dark red, amorphous powder, slightly soluble in alcohol, ether, and chloroform, and in warm glacial acetic acid. It dissolves in solutions of alkali carbonates and hydroxides forming a red liquid. With bromine, it

appears to form a tribromo-derivative,  $C_{20}H_{13}Br_3O_5S$ , and it yields no pure product with phosphorus pentachloride.

When catechol, quinol, and pyrogallol are separately heated with orthosulphoparatoluic acid, phthaleins appear to be formed, but none was isolated in a pure state. Resorcinol and orthosulphoparatoluic acid appear to yield hexaresorcinolparamethylsulphophthalein and octoresorcinolparamethylsulphophthalein, but these are not well-characterised substances.

G. T. M.

**Orcinolsulphophthaleins.** By J. E. GILPIN (*Amer. Chem. J.*, 1894, 16, 528—530; compare preceding abstract).—Diörcinolsulphophthalein is obtained on heating together orcinol (2 mols.) and orthosulphobenzoic acid (1 mol.) at  $180^\circ$ . It is a dark red powder giving a red and green fluorescence in alkaline solution. It is insoluble in water, but dissolves sparingly in alcohol and ether. Attempts to prepare a tetraörcinolsulphophthalein by increasing the proportion of orcinol were without success.

G. T. M.

**Derivatives of Auramine.** By J. FINCKH and M. SCHWIMMER (*J. pr. Chem.*, 1894, [2], 50, 401—445).—*Paramidophenylauramine*,  $NH_2 \cdot C_6H_4 \cdot N \cdot C(C_6H_4 \cdot NMe_2)_2$ , obtained by heating the auramine base with paraphenylenediamine, forms small, golden yellow, lustrous scales, melting at  $221$ — $222^\circ$ . It is moderately soluble in hot alcohol, and is readily decomposed when hydrochloric acid is added to this solution, paraphenylenediamine and tetramethyldiamidobenzophenone being formed. The *hydrochloride* could not be obtained in the crystalline form, but only as an amorphous mass which melts at  $224^\circ$ . The *platinochloride* is a dark brown, granular powder, whilst the *picrate* melts at  $185$ — $186^\circ$  (corr.). The *diacetyl* derivative, obtained by the action of acetic anhydride on the base, is a fine, ochre-yellow powder which melts at  $194$ — $195^\circ$ . When it is heated with carbon bisulphide at  $130^\circ$ , tetramethyldiamidothiobenzophenone is produced along with *diacetamidophenylthiocarbimide*,  $NAc_2 \cdot C_6H_4 \cdot NCS$ , which crystallises in reddish, odourless scales melting at  $195^\circ$ . This substance readily combines with aniline to form *diacetylamidophenylthiocarbimide*,  $NAc_2 \cdot C_6H_4 \cdot NCS \cdot NHPh$ , a compound which crystallises in silver-white, lustrous plates and melts at  $220$ — $221^\circ$ . *Triacetylparamidophenylauramine* is formed in small quantity along with the diacetyl compound. It crystallises in microscopic, greyish-yellow plates which melt at  $257$ — $258^\circ$ . Boiling alcohol converts it into the diacetyl compound, whilst carbon bisulphide produces the diacetamidophenylthiocarbimide already described. *Monobenzoylparamidophenylauramine* forms orange-red prisms, and melts at  $117^\circ$ . The *dibenzoyl* derivative crystallises in hair-like needles, and melts at  $180$ — $181^\circ$ .

The benzoyl derivatives are accompanied by a small amount of a sparingly soluble substance melting at  $326$ — $327^\circ$ , which has the composition  $C_{16}H_8NO$ , and is decomposed by hydrochloric acid at  $150^\circ$  with formation of tetramethyldiamidobenzophenone and benzoic acid. It was found impossible to prepare the corresponding thiocarbimides from the benzoyl derivatives. *Paramidophenylauramine*—

*phenylthiocarbimide*,  $C_{30}H_{31}N_5S$ , obtained by the direct union of its constituents, forms slender, yellow needles melting at  $124-127^\circ$ .

*Paraphenylenediauramine*,  $C_6H_4[N:C(C_6H_4NMe_2)_2]_2$ , is obtained by heating paraphenylenediamine with 2 molecular proportions of auramine. It separates from xylene as a brownish-yellow, crystalline powder, melts at  $311-312^\circ$ , and decomposes at a higher temperature. Hydrochloric acid decomposes it in a similar manner to the monauramines, and carbon bisulphide reacts with it to produce tetramethyldiamidothiobenzophenone and paraphenylenethiocarbimide.

*Orthamidophenylauramine*, prepared by the use of orthophenylenediamine, forms orange-yellow crystals and melts at  $199-200^\circ$ . The *picrate*,  $C_{23}H_{26}N_4C_6H_3N_3O_7$ , melts at  $220-221^\circ$ . *Benzoylorthamidophenylauramine* crystallises in slender, sulphur-yellow needles melting at  $236-237^\circ$ . The base is a primary amido-compound, and not a diimide, since it only reacts with 1 mol. of phenylthiocarbimide, forming *orthamidophenylauraminesphenylthiocarbimide*, which is a yellow, crystalline powder melting at  $166-167^\circ$ .

*Orthophenylenediauramine* may be obtained by the action of orthamidophenylauramine on auramine, but is best prepared in a similar manner to the para-compound. It crystallises from xylene in slender, golden-yellow needles melting at  $305^\circ$ .

*Benzoylauramine*,  $NBz.C(C_6H_4NMe_2)_2$ , is readily formed, and crystallises in long, yellow needles which melt at  $179^\circ$  (corr.), and are not decomposed by continued boiling with water. Acetic acid produces a bluish-violet coloration, whilst sulphuric acid, added to an alcoholic solution, gives a blue coloration. The benzoyl derivative seems not to react with carbon bisulphide.

Auramine, as well as the substituted auramines, forms additive compounds with the thiocarbimides.

*Auraminephenylthiocarbimide*,  $C_{24}H_{26}N_4S$ , crystallises from xylene in microscopic, yellow needles, and melts at  $194-195^\circ$ . Its molecular weight in naphthalene solution is only one-half of that corresponding with the formula given. Dilute acids decompose it, with formation of tetramethyldiamidobenzophenone and phenylthiocarbamide. The thiocarbimide compound undergoes a somewhat complicated reaction when heated with carbon bisulphide at  $150^\circ$ , the products being auramine thiocyanate, tetramethyldiamidothiobenzophenone, phenylthiocarbimide, and thiocarbaniide.

*Auraminemethylthiocarbimide*,  $C_{19}H_{24}N_4S$ , forms odourless, yellow needles, and melts at  $203-203.5^\circ$ . *Auramine-ethylthiocarbimide* also forms yellow crystals melting at  $179^\circ$ . *Auramineallylthiocarbimide* crystallises in yellow prisms, and melts at  $160-161^\circ$ . Carbon bisulphide reacts with it in the same way as with the corresponding phenyl derivative.

A. H.

**Pine Tar.** By A. RENARD (*Compt. rend.*, 1894, **119**, 652—654).—In addition to the terebenthene previously described (Abstr., 1894, i, 612), pine tar contains a new hydrocarbon,  $C_{14}H_{22}$ , which boils at  $250-280^\circ$ . After purification by distillation over sodium, it boils at  $254-257^\circ$ ; sp. gr. at  $0^\circ = 0.9419$ ; refractive index, 1.507. It is a colourless, optically inactive liquid, which rapidly becomes brown

when exposed to air, but is not altered by hydrochloric acid. Bromine attacks it with great violence, forming a colourless, tetrabromo-derivative,  $C_{14}H_{18}Br_4$ , which crystallises from chloroform, but in presence of carbon bisulphide, an unstable dibromide,  $C_{14}H_{22}Br_2$ , is obtained. When the hydrocarbon is passed through a tube heated to dull redness, a small quantity of heptinine is formed. When treated with fuming nitric acid in presence of acetic acid, it yields a nitro-derivative,  $C_{14}H_{21}NO_2$ .

When the hydrocarbon is mixed with twice its volume of ordinary sulphuric acid, there is development of heat, and it is partly converted into a sulphonic derivative, and partly into viscous polymerides, which, when distilled in steam, yield a hydrocarbon boiling at  $250-260^\circ$ , and if the latter is treated with fuming sulphuric acid until no more of it dissolves, a hydrocarbon,  $C_{14}H_{26}$ , boiling at  $250-253^\circ$ , is obtained; this is not affected by fuming sulphuric acid, fuming nitric acid, or bromine in the cold. The sulphonic acid is a gummy substance, soluble in water, alcohol, or ether, and precipitated from its aqueous solutions by sulphuric or hydrochloric acids or sodium chloride. Its ammonium salt is very soluble in water, and yields a fluorescent solution, from which it is precipitated as a gummy mass by sodium chloride. The barium salt,  $Ba(C_{14}H_{21}SO_3)_2$ , is insoluble in water.

If the hydrocarbon,  $C_{14}H_{22}$ , is gently heated with a mixture of sulphuric acid and alcohol, a distinct blue coloration appears, and this reaction, according to Maquenne, is characteristic of the hydrides of benzene and its homologues. The other properties of the hydrocarbon also indicate that it is related to these hydrides, and it may be regarded as diheptenyl  $(C_7H_{11})_2$ , or ditolyl octohydride,  $C_7H_{11} \cdot C_7H_{11}$ . C. H. B.

**Reuniol.** By A. HESSE (*J. pr. Chem.*, 1894, [2], 50, 472—479).—Oil of geranium, from the island of Réunion, contains a terpene-alcohol which is different from geraniol. It may be obtained by heating the oil with alcoholic potash at  $100^\circ$ , to decompose the ethereal salts which it contains, and then etherifying the alcoholic constituents by heating with camphoric anhydride. The non-alcoholic substances present may then be removed by distillation with steam, and the alcoholic constituents thus left in a state of greater purity. Reuniol obtained in this way boils at  $225.5-226^\circ$ , has sp. gr. =  $0.865$  at  $20^\circ$ , and the rotatory power of  $1^\circ 45'$  (100 mm. tube). Its formula is probably  $C_{16}H_{18}O$ , although the numbers obtained by analysis do not agree very sharply with this, probably owing to the presence of water, which is very difficult to remove. The acetate boils at  $124-125^\circ$  (17 mm.), and has sp. gr. =  $0.899$  at  $20^\circ$ . Reuniol does not appear to form a definite compound with calcium chloride, and can thus be separated from geraniol. It has been detected in geranium oil from many sources, the French, African, and Spanish oils all being found to contain it. A substance possessing very similar properties has been described by Barbier (this vol., i, 4), who, however, does not seem to have obtained it free from non-alcoholic impurities. A. H.



**Hydroxymethylene Compounds from Ketones of the Terpene Series.** By O. WALLACH (*Ber.*, 1895, **28**, 31–34; compare L. Claisen, this vol., i, 62).—The formation of hydroxymethylene compounds from carvone, thujone, and hydrocarvone, indicates the presence of the group  $-\text{COMe}$  in these ketones; fenchone, on the other hand, does not yield a derivative.

*Hydroxymethylenecarvone*,  $\text{C}_8\text{H}_{12}$   $\begin{smallmatrix} \text{C:CH}\cdot\text{OH} \\ | \\ \text{CO} \end{smallmatrix}$ , is prepared by the action of sodium and amylic formate on an ethereal solution of *d*-carvone. It boils at  $132^\circ$  under a pressure of 12 mm., and decomposes very readily on exposure to air; an intense violet-red coloration is developed by ferric chloride.

*Hydroxymethylenethujone*,  $\text{C}_{11}\text{H}_{18}\text{O}_2$ , is obtained from thujone in a similar manner; it melts at  $40^\circ$ , and boils at  $115\text{--}118^\circ$  (16 mm.).

The isomeride of camphor, obtained by heating the product of the oxidation of terpineol,  $\text{C}_{10}\text{H}_{20}\text{O}_3$ , with dilute sulphuric acid (Abstr., 1894, i, 44), also gives rise to a hydroxymethylene compound.

M. O. F.

**Camphoric Acid.** By W. A. NOYES (*Amer. Chem. J.*, 1894, **16**, 500–511; compare Abstr., 1894, i, 339).—The dihydroamidocampholytic acid, previously obtained (*loc. cit.*), forms the following derivatives. A *hydrochloride*, which crystallises from hot, concentrated solutions in long, stout needles, and melts and decomposes at  $261\text{--}262^\circ$ ; the crystals show no tendency to a concentric grouping, and in this respect differ very markedly from those of the hydrochloride of the isomeric amidolauroic acid (m. p.  $303\text{--}305^\circ$ ). The *nitrate* crystallises in long needles, and melts with decomposition at  $212\text{--}213^\circ$ ; the *platinochloride*, in dark, orange-red plates.

Attempts to obtain an amine by distilling dihydroamidocampholytic acid with quicklime, resulted in the formation of an inner *anhydride* of the acid, having the formula,  $\text{C}_8\text{H}_{14}$   $\begin{smallmatrix} \text{CO} \\ | \\ \text{NH} \end{smallmatrix}$ . It is a wax-

like substance, melts at  $188\text{--}189^\circ$ , boils without decomposition at  $285\text{--}287^\circ$ , and dissolves readily in ordinary solvents.

Campholytic acid forms a dibromide, which melts at  $113\text{--}114^\circ$  (compare Walker, *Trans.*, 1893, 499), and is decomposed by ammonia and sodium carbonate, giving an oil which is insoluble in acids and alkalis. It forms insoluble zinc and silver salts (compare Walker, *loc. cit.*). The former is obtained in a semi-crystalline form when a solution of zinc chloride is added to a solution of the sodium salt.

Amidolauroic acid is obtained on heating  $\alpha$ -camphoramic acid with sodium hypobromite in the same way as dihydroamidocampholytic acid is obtained from  $\beta$ -camphoramic acid, and is best isolated by conversion into the *hydrochloride*. The latter crystallises from water in well-defined needles, which have a strong tendency to form concentric groups; it melts at  $303\text{--}305^\circ$ , and is more sparingly soluble than the isomeric hydrochloride of dihydroamidocampholytic acid. The *platinochloride*,  $(\text{C}_9\text{H}_{17}\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in orange-red, microscopic, six-sided plates, and is more sparingly soluble than its

isomeride. The *anhydride* in most respects resembles its isomeride, but melts at 203°.

The study of the products of decomposition of the hydrochloride of amidolauroic acid by sodium nitrite is not yet complete, but the author regards his work as being in accordance with the supposition made by Walker, that camphoric acid contains the group  $\text{COOH}\cdot\text{CH}\cdot\text{CR}\cdot\text{COOH}$ , and with the relative position ascribed to the carbonyl and methylene groups in the formula for camphor proposed by Armstrong. G. T. M.

**Camphoronic acid and its Optical Isomerides.** By O. ASCHAN (*Ber.*, 1895, **28**, 16—21).—Ordinary camphoronic acid,  $\text{C}_9\text{H}_{14}\text{O}_6$ , is lævorotatory, having  $[\alpha]_D = -26.9$ ; it melts and evolves gas at 158°, and 16.9 parts of it dissolve at 20° in 100 parts of water. Dextrorotatory camphoronic acid was prepared from the residues in the preparation of *l*-camphoric acid from *l*-borneol, from 90 grams of which, after a tedious process of purification, 6 grams of the acid were obtained. It has  $[\alpha]_D = +27.05$ ; it melts at 158—159°, gas being evolved; 16.74 parts dissolve in 100 parts of water at 20°; in appearance it resembles the *l*-isomeride, and a like resemblance is exhibited by the isomeric calcium salts, which both contain  $8\text{H}_2\text{O}$  when dried in a vacuum,  $12\text{H}_2\text{O}$  when dried in the air. When the two isomeric acids are mixed in aqueous solution, the inactive racemic acid is formed; this has quite different properties. It crystallises in large, square plates, instead of in needles; melts at 172°; and dissolves only to the extent of 3.72 parts in 100 of water at 20°; the barium salt is very soluble in water, whereas the barium salts of the two active acids are almost insoluble.

By the action of bromine on camphoronic chloride, a compound is obtained which is probably  $\text{COOH}\cdot\text{C}_9\text{H}_{10}\text{Br}\cdot(\text{CO})_2\text{O}$ , being both an acid and an acid anhydride; it melts at 158°. Boiling water removes hydrogen bromide from it, yielding a (? lactonic) acid, melting at 208—209°; another acid melting at 240° is formed in addition. It also yields an anil melting at 171—172°. These compounds are undergoing further investigation. C. F. B.

**Balsam of Tolu.** By P. OBERLAENDER (*Arch. Pharm.*, 1894, **232**, 559—600).—Balsam of Tolu consists almost entirely of a mixture of ethereal salts of benzoic and cinnamic acids; partly (7.5 per cent.) the benzylic salts, with which a little vanillin is associated, the rest those of a resin alcohol; this alcohol is prepared from the ethereal solution of the balsam by first extracting the resinous salts with cold alkali and precipitating them with carbonic anhydride, and then repeatedly hydrolysing them with alkali, the alcohol being precipitated after each dissolution with hot hydrochloric acid. The final purification is effected by repeated precipitation with acid from ammoniacal solution.

*Toluresinotannol*,  $\text{C}_{17}\text{H}_{18}\text{O}_5$ , a lower homologue of peruresinotannol, is a dark brown, neutral powder, having no taste or odour; it does not soften when heated, but decomposes at 100° without melting (the balsam melts at 65°). It is closely related to the tannins, as it gives

colour reactions with ferric chloride and potassium dichromate, and precipitates with lead acetate and gelatin; a characteristic black coloration is obtained with hydrochloric acid. The molecule contains a hydroxyl group, as the tannol forms alkali and acidyl derivatives; it also contains a methoxy-group, removable by hydriodic acid; the constitutional formula is therefore  $\text{OH} \cdot \text{C}_{16}\text{H}_{14}\text{O}_3 \cdot \text{OMe}$ . As the acidyl derivatives do not show the above phenolic reactions, and the tannin does not interact with phenylhydrazine or hydroxylamine, the remaining oxygen is neither in the ketonic nor the aldehydic nor the hydroxylic form. On oxidation, reduction, and bromination, the tannin yields indefinite products; with nitric acid, however, picric and oxalic acids are obtained. When fused with caustic potash, it yields acetic and protocatechuic acids and a trace of valeric acid; when distilled with zinc dust, low phenols and naphthalene. The potassium derivative,  $\text{C}_{17}\text{H}_{17}\text{KO}_5$ , forms white, amorphous flocks. The acetyl derivative,  $\text{C}_{17}\text{H}_{17}\text{AcO}_5$ , is an ochre-yellow, crystalline powder; like the other acidyl derivatives, it is hydrolysed into its proximate constituents by alkalis. The benzoyl derivative is a yellowish-brown, amorphous powder; the cinnamoyl derivative, a greyish-brown powder, which does not resemble the original resin. JN. W.

**The Sugar of Indican.** By C. J. VAN LOOKEREN (*Landw. Versuchs-Stat.*, 1894, 45, 195—200).—The author previously expressed the opinion (this vol., i, 96) that the sugar obtained from indican, which Schunck calls indiglucin, is dextrose; this is now shown to be the case. Owing to the great ease with which indican decomposes, it was found best to treat the fresh sap of indigofera leaves with sulphuric acid. The resulting sugar was identified as dextrose by means of the osazone, its rotatory power, and its reaction with nitric acid. A small quantity of levulose was also found, but this was present in the fresh sap. N. H. J. M.

**Randia Dumetorum.** By M. VOGTHER (Arch. Pharm., 1894, 232, 489—532).—The fruit of the bushy gardenia (*Randia dumetorum*, Lamarck) is in popular use in India, where the plant is known as *Gelaphal*, as an emetic and remedy for dysentery. In addition to the substances described later, a minute quantity of an alkaloid was isolated, but not characterised or identified, and a small amount of lead (0.02 per cent.) was invariably present.

*Randiasaponin*, a glucoside, forms yellowish plates, or a white, amorphous powder, and melts and decomposes at about  $250^\circ$ . It loses 11.4 per cent. of water at  $100^\circ$ ; the percentage composition of the dry substance is C, 55.52; H, 8.72; O, 35.76. It is not hygroscopic, but dissolves in water to a neutral solution, which froths readily. It is reprecipitated from this solution by moderately strong hydrochloric or sulphuric acid, and is also thrown down by lead acetate and basic acetate as a gelatinous compound, which serves for its purification. It does not reduce alkaline copper solution, except after prolonged hydrolysis with dilute hydrochloric acid, when it is converted into randiasapogenin and two sugars. The osazone of one of these is insoluble in ether, crystallises in yellow crusts, and melts

at 166—167°, whilst that of the other is soluble in ether and amorphous, and melts at 176—177°. Randiasaponin, like quillayasapotoxin, has the property of dissolving red blood corpuscles to a clear solution.

*Randiasapogenin*,  $C_{26}H_{50}O_9$  (?), the product of the hydrolysis of randiasaponin, forms a friable mass, little soluble in water. It decomposes without melting, the chief product being a substance crystallising in colourless needles. Moist randiasapogenin dissolves in strong sulphuric acid to a yellow solution, which shows a characteristic green fluorescence.

*Randic acid*,  $C_{30}H_{52}O_{10}$ , appears to be a monobasic acid of the series  $C_nH_{2n-8}O_{10}$ , characterised by Kobert as the saponin series, and exists, apparently, in loose combination with randiasaponin. It crystallises from alcohol in white, nodular masses, and melts at 208—210°. It is sparingly soluble in water and ether, freely in alcohol, acetic acid, and concentrated sulphuric acid; solutions of the alkali salts froth very readily. The *potassium* salt is insoluble in alcohol. The *calcium*, *barium*, *ferrous*, *ferric*, *copper*, *lead*, *mercurous*, and *mercuric* salts are mentioned. Randic acid resembles quillayic acid in dissolving red blood corpuscles without destroying the colouring matter, and in precipitating albumins and peptones. To these properties, and the similar property of randiasaponin, the poisonous character of the fruit is probably due.

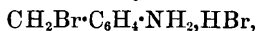
*Randiatannic acid* exists in small quantity in the pericarp, and is a brown, very hygroscopic mass, which is freely soluble in ether, as well as in water and alcohol. It gives a green coloration with ferric chloride, and a yellow precipitate with basic lead acetate, and reduces alkaline copper solution.

One of the products of the decomposition of randiatannic acid appears to be *randia-red*,  $C_{33}H_{34}O_{26}$ , a substance to which the brown colour of the pericarp of the fruit is due; this is precipitated by acids from the alkaline extract as a brown powder, which is insoluble in water, alcohol, and ether, but easily soluble in alkalis. The solutions give reddish precipitates with lead acetate and alum. A brownish-red colouring matter, probably the *ammonium*-derivative, is precipitated by ammonia from the acid mother liquor; it forms a harsh mass resembling asphalt, and is soluble in hot water; it is decomposed by caustic soda with evolution of ammonia.

*Randia fat* is a yellowish-green substance of the consistence of butter; it melts at 28—29°, and its sp. gr. is 0.9175 at 20°. The acid number is 13.8; the ester number, 146.4; the saponification number, 160.2; and the iodine number, after two hours, 43.24.

JN. W.

**Halogenised Amines.** By S. GABRIEL and T. POSNER (*Ber.*, 1894, 27, 3509—3525).—When orthamidobenzyl alcohol (15 grams) is heated with fuming hydrobromic acid (40 c.c.) for an hour at 100°, the *hydrobromide* of orthamidobenzyl bromide,



is formed. The *hydrochloride* of orthamidobenzyl chloride is prepared in a similar manner, but neither salt yields the free base on

treatment with alkali, a colourless precipitate of orthobenzyleneimide,  $(C_7H_7N)_x$  being thrown down.

$\mu$ -Methylphenopentoxazole,  $C_6H_4 < \begin{smallmatrix} CH_2 \cdot O \\ N = CMe \end{smallmatrix}$ , is obtained in the form of the *hydrobromide* when the hydrobromide of orthamidobenzyllic bromide is heated for a few minutes with acetic anhydride; the salt melts at  $170-172^\circ$ , and has an acrid taste. The free base is a yellow oil, which rapidly decomposes when distilled alone or in a current of steam, but a portion remains unchanged and boils at  $230^\circ$ ; the *picrate* melts at  $146-149^\circ$ . Methylphenopentoxazole hydrobromide in aqueous solution undergoes spontaneous conversion into the hydrobromide of orthamidobenzyllic acetate (Söderbaum and Widman, Abstr., 1889, 972), of which the *picrate* crystallises in short prisms and melts at  $99^\circ$ .

$\mu$ -Methylphenopentthiazole,  $C_6H_4 < \begin{smallmatrix} CH_2 \cdot S \\ N = CMe \end{smallmatrix}$ , is obtained by the action of phosphorus pentasulphide on the hydrobromide of methylphenopentoxazole; it melts at  $45-46^\circ$ , and boils at  $265-267^\circ$  under a pressure of 771 mm. It is also obtained by heating orthamidobenzyllic chloride hydrochloride or orthamidobenzyllic alcohol with acetic anhydride, and subsequent treatment with phosphorus pentasulphide; the same base is produced on heating a mixture of the hydrochloride of orthamidobenzyllic chloride and thioacetamide for a quarter of an hour at  $100^\circ$ . The *platinochloride* forms orange-yellow needles, and the *dichromate* crystallises in lustrous, reddish-yellow needles; the *picrate* blackens at  $170^\circ$  and melts at  $178^\circ$ . Orthamidobenzyllic sulphide is formed when methylphenopentthiazole is heated with fuming hydrochloric acid for two hours at  $180^\circ$ ; it melts at  $81-82^\circ$ . The *formyl* derivative crystallises in snow-white needles which melt at  $163^\circ$ , and the *acetyl* derivative forms silky needles which melt at  $209^\circ$ ; when this substance is heated on the water bath with phosphorus pentachloride, methylphenopentthiazole is formed.

$\mu$ -Ethylphenopentoxazole,  $C_6H_4 < \begin{smallmatrix} CH_2 \cdot O \\ N = CEt \end{smallmatrix}$ , is obtained similarly to the methyl derivative from orthamidobenzyllic bromide and propionic anhydride. The *picrate* melts at  $138-139^\circ$ .

Orthobenzamidobenzyllic chloride is formed when the hydrochloride of orthamidobenzyllic chloride is added to benzoic chloride which is nearly boiling; it separates from alcohol in silky needles which melt at  $124-125^\circ$ . When this substance is heated with phosphorus pentasulphide,  $\mu$ -phenylphenopentthiazole,  $C_6H_4 < \begin{smallmatrix} CH_2 \cdot S \\ N = CPh \end{smallmatrix}$ , is formed; it crystallises from methylic alcohol in yellowish needles which melt at  $55-58^\circ$ , and the *picrate* melts at  $176-177^\circ$ . The base is also obtained by heating a mixture of the hydrobromide of orthamidobenzyllic bromide and thiobenzamide at  $100^\circ$ .

Orthobenzamidobenzylaniline,  $NHPh \cdot CH_2 \cdot C_6H_4 \cdot NHBz$ , is formed on heating orthamidobenzyllic chloride with aniline; it crystallises in colourless needles which melt at  $113-114^\circ$ . This substance is isomeric with orthamidobenzylbenzanilide, which melts at  $119^\circ$ .

The following halogenised amines will form the subject of a later communication— $\beta$ -chloro-,  $\beta$ -bromo-, and  $\gamma$ -chloro-butylamine,  $\gamma$ -chloro-, and  $\gamma$ -bromo-hexylamine.

M. O. F.

**Derivatives of Furazan.** By L. WOLFF (*Ber.*, 1895, 28, 69—74).—The author has succeeded in preparing the anhydrides of dimethylglyoxime and methylglyoximecarboxylic acid, although Hantzsch (*Abstr.*, 1892, 693) and Nussberger (*Abstr.*, 1892, 1175) were unable

to obtain these compounds. *Dimethylfurazan*,  $O < \begin{smallmatrix} N: CMe \\ N: CMe \end{smallmatrix}$ , is formed

when dimethylglyoxime is boiled with aqueous soda, but is best prepared by heating it with water at  $160^\circ$ . It is a colourless liquid of sp. gr. 1.054 at  $15^\circ$ , boils without decomposition at  $156^\circ$ , and when cooled solidifies to a crystalline mass, melting at  $-7^\circ$ . It is volatile with steam, and is exceptionally stable towards acids and alkalis. When treated with potassium permanganate in presence of sulphuric acid,

it is converted into *methylfurazancarboxylic acid*,  $O < \begin{smallmatrix} N: C \cdot COOH \\ N: CMe \end{smallmatrix}$ ,

which crystallises with  $1H_2O$  in large, lustrous plates, melting at  $39^\circ$ . The anhydrous acid melts at  $74^\circ$ , and absorbs water from the air. The *calcium* salt crystallises in plates, the *silver* salt in needles. Methylfurazancarboxylic acid is converted, by oxidation with potassium permanganate, into *furazandicarboxylic acid*,  $O < \begin{smallmatrix} N: C \cdot COOH \\ N: C \cdot COOH \end{smallmatrix}$ ,

which crystallises in large, vitreous prisms, melting and evolving gas, at  $178^\circ$ . The *calcium* salt crystallises in white, lustrous needles, whilst the *silver* salt is a crystalline powder. Both the acid and its salts very readily decompose when they are boiled with water, carbonic anhydride being evolved, and cyanoximidoacetic acid formed. The following reactions are due to this change. The colourless solutions of the calcium and alkali salts become yellow when boiled, and then give a yellow precipitate with silver nitrate solution. Copper acetate produces no precipitate, but, when the blue solution is boiled, it becomes green, and deposits crystals of copper cyanoximidoacetate.

*Methylethylfurazan* is a mobile, neutral liquid, boiling at  $170.5^\circ$ .

The author has made a number of unsuccessful attempts to convert dimethylglyoxime into an isomeric compound by the action of hydrogen chloride in various solvents, of caustic soda, and of sulphuric acid.

A. H.

**Phenyl-Derivatives of Pyrazole.** By E. BUCHNER (*Ber.*, 1894, 27, 3247—3250).—In conjunction with Dessauer and Fritsch (*Abstr.*, 1893, i, 281, 282), the author has shown that two phenylpyrazoles, melting at  $228^\circ$  and  $78^\circ$  respectively, are obtained from ethylic diazoacetate and ethylic cinnamate, in both of which the phenyl group is combined with a carbon atom. These were regarded as 5- and 4-pyrazoles, but recent syntheses of the latter by Knorr and Sjöllerua (*Abstr.*, 1894, i, 546) have shown that it must be either 3- or 5-pyrazole. Knorr and Sjöllerua regard the compound melting at  $228^\circ$  as the 4-derivative, its synthesis by Rothenburg from hydrazine hydrate

and benzoylacetalddehyde, however, is not in agreement with this supposition, but shows that this also must be a 3- or 5-derivative; this is also borne out by the fact that the corresponding dicarboxylic acid, when heated with resorcinol, gives a fluorescent solution on the addition of ammonia. A definite decision as to which is the 3-derivative and which the 5-derivative is not at present possible, but the author does not agree with Knorr's view (Abstr., 1894, i, 543), that the positions 3- and 5- in the pyrazole ring are identical. H. G. C.

**Action of Phenylhydrazine on Ethylic Ethoxymethylene-malonate.** By L. CLAISEN and E. HAASE (*Ber.*, 1895, 28, 35—41).—This condensation gives rise to the *phenylhydrazide*,



which melts at 112°. When this substance is heated in an oil bath at 170—175°, the ethylic salt of 1:5:4-phenylpyrazolonecarboxylic acid is formed (compare Ruhemann and Morrell, *Trans.*, 1892, 793). On boiling this salt for some hours with aqueous caustic soda (3 mols.), 1:5-phenylpyrazolone is formed, which melts at 118—119°.

1:5-Phenylpyrazolone closely resembles Knorr's 1:3:5-phenylmethylpyrazolone in properties. The *hydrochloride* melts at 165°; the *benzylidene*- and *isonitroso*-derivatives melt at 170° and 160° respectively.

The constitution of 1:5-phenylpyrazolone has been the subject of recent discussion, and the author shows that it is best represented by the formula  $\begin{array}{c} \text{NPh}\cdot\text{CO} \\ | \\ \text{N}=\text{CH} \end{array} > \text{CH}_2$ , already put forward by Stolz.

M. O. F.

**Derivatives of Tetrazole.** By M. FREUND and H. HEMPEL (*Ber.*, 1895, 28, 74—81).—4-Phenylthiosemicarbazide is a base, and forms a *hydrochloride*, which crystallises in compact needles, melting at 169°. When this is dissolved in dilute acid and treated with potassium nitrite solution, a compound, which is probably 4-phenyl-3-thio-tetrazoline,  $\text{N} \begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{NPh} \\ \text{NH}\cdot\text{CS} \end{array}$ , is precipitated. It crystallises from alcohol in compact needles, which decompose violently at 142—145°. It dissolves in aqueous alkalis when gently heated, and can be recovered by the addition of acid; if, however, the solution be more strongly heated, the isomeric phenyltetrazolethiole is formed. Ammoniacal silver oxide added to an alcoholic solution of the tetrazoline produces the silver salt of the isomeric tetrazole.

4-Phenyltetrazole-3-thiole,  $\text{N} \begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{NPh} \\ \text{N}\cdot\text{C}\cdot\text{SH} \end{array}$ , crystallises in slender, matted needles, which decompose at 147—150°. It dissolves without alteration in cold sulphuric acid or boiling hydrochloric acid. The *silver* salt,  $\text{CN}_4\text{PhSAg}$ , is an amorphous, white mass. When treated with methylic iodide, it is converted into *phenyltetrazolemethylthiole*,  $\text{CN}_4\text{Ph}\cdot\text{SMe}$ , which crystallises in cubes, melting at 84°. The same compound is obtained when the tetrazole is heated with sodium ethoxide and methylic iodide. When oxidised with potassium permanganate, the tetrazole is converted into 4-phenyltetrazole-3-sulphonic

acid, of which the *potassium* salt,  $\text{CN}_4\text{Ph}\cdot\text{SO}_3\text{K}$ , is soluble in alcohol and melts at  $242^\circ$ .

4-*Phenyl-3-hydroxytetrazole*,  $\text{CN}_4\text{Ph}\cdot\text{OH}$ , accompanies the sulphonic acid just described. It crystallises from alcohol in slender, matted needles, melting at  $185\text{--}186^\circ$ . Its *potassium* salt,  $\text{C}_7\text{H}_5\text{N}_4\text{OK}$ , is also soluble in alcohol. Oxidation, by means of nitric or nitrous acid, ferric chloride, or hydrogen peroxide, converts the tetrazole into the corresponding *bisulphide*,  $\text{S}_2(\text{CN}_4\text{Ph})_2$ , which forms flat, rhombic crystals, and decomposes at  $145\text{--}148^\circ$ . It is insoluble in cold aqueous alkalis, but dissolves in them on warming, reduction to the tetrazole taking place. A similar reduction also occurs when it is treated with ammoniacal silver oxide.

The relations of the tetrazoline and tetrazole compounds are best expressed by the formulæ given above, the existence of the mercaptan group in the tetrazole being proved by its behaviour on oxidation. It will be noticed that the two formulæ represent what are usually recognised as tautomeric forms of the same substance. A. H.

**Vellosine: an Alkaloid from Pereiro Bark** ("Geissospermum Vellosii"). By M. FREUND and C. FAUVET (*Annalen*, 1894, 282, 247—267).—A preliminary investigation of the so-called geissospermine, manufactured by Trommsdorff (Abstr., 1833, i, 446), showed that this compound was not identical with Hesse's geissospermine (Abstr., 1880, 675). Hesse (Abstr., 1894, i, 155) believes that Trommsdorff's base is identical with a third alkaloid previously isolated by him (*loc. cit.*) from pereiro bark. There are, however, on the market, two sorts of pereiro bark: a thin, bast-like variety and a thicker kind; it is from the latter that Trommsdorff prepares his alkaloid. Hesse has not stated which of the two varieties he worked with. The authors now propose the name *vellosine* for Trommsdorff's base, and *apovellosine* for the amorphous base obtained from it (Abstr., 1893, i, 466).

*Vellosine*,  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4$  (m. p.  $189^\circ$ ), has already been partially described (*loc. cit.*). The base is soluble in chloroform and hot benzene, but insoluble in water, and dissolves in concentrated nitric acid with decomposition and the production of a purple-red coloration; it forms rhombic, hemihedral crystals,

$$a : b : c = 0.9703 : 1 : 0.6140,$$

has a specific rotatory power in a chloroform solution of about 10 per cent. concentration of  $[\alpha]_D = +22.8$  at  $23^\circ$ . Its molecular weight, determined by the ebullioscopic method, is in agreement with the above formula, and Zeisel's method reveals the presence of two methoxyl groups. As vellosine is easily converted into apovellosine by dilute acids (see below), heating must be avoided in the preparation of its salts. The *hydrochloride*,  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4\cdot\text{HCl} + \text{H}_2\text{O}$ , commences to soften at  $170^\circ$ , and melts in its water of crystallisation at  $180^\circ$  with frothing; subsequently, however, it again solidifies, and then melts and decomposes at  $240^\circ$ . If the salt is previously dehydrated at  $120^\circ$ , it melts at  $245\text{--}248^\circ$ . The *platinochloride* is a crystalline powder of melting point  $80^\circ$ ; when heated with water, it



decomposes with the production of a violet coloration. The *hydrobromide* crystallises in lustrous needles with  $1\text{H}_2\text{O}$ ; it melts at  $194\text{--}195^\circ$ , which value is the same for the anhydrous salt. The *hydriodide* crystallises with  $1\text{H}_2\text{O}$ , commences to soften at  $210^\circ$ , and melts at  $217\text{--}218^\circ$ . *Vellosine hydrogen sulphate*,



melts at  $210^\circ$ , and the *nitrate* decomposes at  $225^\circ$ . The *methiodide*,  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4, \text{MeI}$ , melts at  $264^\circ$ .

*Apovellosine*,  $\text{C}_{46}\text{H}_{54}\text{N}_4\text{O}_7$ , is prepared by boiling a solution of vellosine in excess of hydrochloric acid of 1.1 sp. gr. for five minutes, and precipitating with soda; the base is amorphous, hygroscopic, very soluble in most organic solvents, and melts, according to the way it is heated, between  $60^\circ$  and  $70^\circ$ . If a trace of the base is dissolved in a drop of concentrated sulphuric acid containing some nitric acid, a beautiful violet colour is developed as the solution absorbs water: a solution in hydrochloric acid gives a carmine-red coloration on the addition of ferric chloride, which changes to violet on adding soda, but is destroyed by an excess of the latter. The formula given above for the base is supported by the ebullioscopic method; Zeisel's method shows that apovellosine contains four methoxyl groups. The *hydriodide*,  $\text{C}_{46}\text{H}_{54}\text{N}_4\text{O}_7, 4\text{HI} + 4\text{H}_2\text{O}$  sinters at  $160^\circ$ , and melts with decomposition at  $253\text{--}254^\circ$ . The *hydrobromide* (anhydrous) melts and decomposes at  $210^\circ$ ; the *methiodide*,  $\text{C}_{46}\text{H}_{54}\text{N}_4\text{O}_7, 2\text{MeI}$ , melts at  $265^\circ$ . The *nitrate* and *platinochloride* are unstable, and were not isolated.

*Apovellosol hydrobromide*,  $\text{C}_{42}\text{H}_{46}\text{N}_4\text{O}_7, 4\text{HBr} + 5\text{H}_2\text{O}$ , is produced, together with methylic bromide and water, when vellosine is boiled with concentrated hydrobromic acid; it separates from hot water in stout crystals, and melts at  $245^\circ$ . A solution acidified with hydrochloric acid gives a beautiful, carmine-red coloration with ferric chloride, which, on the addition of soda, changes to violet and then vanishes; if the precipitated ferric oxide is now dissolved in acetic acid, a colourless solution is formed, which again becomes carmine-red on adding hydrochloric acid. When concentrated potash is added to a solution of the hydrobromide, an oil separates which is probably a potassium derivative of apovellosol. The *hydriodide* crystallises with  $5\text{H}_2\text{O}$ ; this hydrate melts at  $235^\circ$ ; a specimen crystallised from aqueous alcohol melted at  $265^\circ$ .

*Apovellosidine*,  $\text{C}_{42}\text{H}_{54}\text{N}_4\text{O}_6$ , obtained by evaporating a solution of apovellosine with potassium hydroxide, crystallises from alcohol in colourless needles, and melts at  $154^\circ$ ; the compound contains four methoxyl groups. The *hydrobromide*,  $\text{C}_{42}\text{H}_{54}\text{N}_4\text{O}_6, 3\text{HBr} + 6\text{H}_2\text{O}$ , melts at  $235^\circ$ ; the *platinochloride* melts at  $203^\circ$ , and the *methiodide*,  $\text{C}_{42}\text{H}_{52}\text{N}_4\text{O}_5, 2\text{MeI}$ , melts at  $262^\circ$ . When vellosine is heated with alkali, a compound melting at  $145^\circ$  is obtained; it is not identical with apovellosidine.

Vellosine is toxic, the lethal dose being 0.15 gram in the case of rabbits; death occurs by the weakening of the respiratory centre. A short account of the further physiological action of the base is given in the paper.

A. R. L.

**Cadaverine and Choline from Putrid Horseflesh.** By W. GULEWITSCH (*Zeit. physiol. Chem.*, 1894, **20**, 287—305).—These two substances were obtained from putrid horseflesh in quantity, and a number of their compounds were prepared, and analysed. Among these may be mentioned the compound of cadaverine and mercuric chloride,  $C_5H_{12}N_2 \cdot 2HCl \cdot 4HgCl_2$ ; at  $135^\circ$ , this loses 18.33 per cent. of mercuric chloride. The platinochloride,  $C_5H_{14}N_2 \cdot H_2PtCl_6$ , was prepared. The crystalline form of different ptomaine derivatives appears to vary a good deal.

The name *ptomatine* is suggested as more grammatically correct than ptomaine. W. D. H.

**Ash-free Albumin.** By K. BÜLOW (*Pflüger's Archiv*, 1894, **58**, 207—221).—Ash-free albumin was prepared by Harnack's method from various proteid sources; and although the original proteids differ in their properties, the ash-free product does not. It is insoluble in water, and like amido-acids, it forms, with acids and bases, salts soluble in water; it appears to form, with bases, two categories of compounds.

The acid solutions are very sensitive to neutral salts, a small addition producing precipitation; the alkaline solutions are indifferent to neutral salts. In this direction, the sulphates of the alkali metals act most strongly, then the nitrates, then the chlorides. The specific rotatory power of proteids is markedly altered by small admixtures of other substances. W. D. H.

**Ferratin: its Dietetical and Therapeutical Employment.** By O. SCHMIEDEBERG (*Chem. Centr.*, 1894, i, 741).—The iron compounds of albumin, like other iron compounds, are at once blackened by ammonium sulphide in alkaline solution. If, however, alkaline solutions of such iron albuminates are kept some time, or are heated for a short time, they are not at once blackened by ammonium sulphide, although they are blackened by it after the lapse of some time. Iron compounds which are not at once blackened by ammonium sulphide are obtained from many organic compounds which contain hydroxyl, such as tartaric acid, citric acid, mannitol, and glycerol. *Ferratin*, a "ferrialbuminic acid" containing 6 per cent. of iron, is obtained by boiling pig's liver with water, and adding tartaric acid to the cold filtrate. The ferratin contained in the liver is the source of iron for the formation of blood, and its disappearance from the liver can be detected in cases of deficiency of iron and loss of blood. Iron salts are, as a rule, difficult to assimilate; ferratin, however, after repeated doses, is not injurious either to the intestines or kidneys; and much larger quantities of iron may be injected directly into the blood in the form of ferratin than in the form of iron salts. E. C. R.

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## Organic Chemistry.

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**Sodionitroethane.** By VICTOR MEYER (*Ber.*, 1895, **28**, 202—204).—The author traverses Nef's statements (this vol., i, 3). When sodionitroethane is decomposed with ice-cold, dilute sulphuric acid, it is converted to the extent of over 60 per cent. into nitroethane, and only a small quantity of nitrous oxide is evolved; if acetic acid is used, no nitrous oxide is evolved. It must thus be a true derivative of nitroethane, and cannot have a quite dissimilar constitution. C. F. B.

**Hydration of Acetylene: Formation of Paraldehyde.** By ALEXANDRE DESGREZ (*Bull. Soc. Chim.*, 1894, [3], **11**, 362—366).—Purified wood charcoal, at a moderate temperature, absorbs acetylene, and the latter, on treatment with water at 325°, is converted into an aldehyde, since the product restores the colour to reduced rosaniline. A better yield is obtained by heating acetylenedicarboxylic acid with water at 320—330° for half an hour; on distilling the product at a low temperature, a considerable quantity of a liquid passes over, which restores the colour to reduced rosaniline, and can be converted into silver acetate; as the temperature was above 40°, it was probably paraldehyde. On passing the more volatile portions of the product into a solution of ammonia in ether, a small quantity of aldehyde-ammonia was formed. JN. W.

**Hydration of Allylene.** By ALEXANDRE DESGREZ (*Bull. Soc. Chim.*, 1894, [3], **11**, 391—394).—When tetrolic acid,  $\text{CMe:C}\cdot\text{COOH}$  (from  $\beta$ -chlorocrotonic acid), is heated with water at 325—330° for half an hour, the liberated allylene is converted into acetone, which may be isolated by means of the sodium hydrogen sulphite compound, and recognised in the usual manner. At a higher temperature, mesitylic oxide is probably formed, but not propaldehyde. JN. W.

**Action of Reducing Agents on Potassium Nickelocyanide.** By THOMAS MOORE (*Chem. News*, 1895, **71**, 81—82).—See this vol., ii, 168.

**Preparation of Potassium Ferricyanide.** By M. S. WALKER (*Amer. Chem. J.*, 1895, **17**, 68).—Twenty-six grams of potassium ferrocyanide are dissolved in 200 c.c. of cold water, 8 c.c. of strong hydrochloric acid added, and then a solution of 2 grams of potassium permanganate in 300 c.c. of water until oxidation is complete. On neutralising with chalk or barium carbonate, and evaporating, crystals of the pure ferricyanide are obtained. L. T. T.

**Oxidation of Alcohols by Fehling's Solution. Transformation of Propionic into Lactic acid.** By FERNAND GAUD (*Compt. rend.*, 1894, **119**, 862—863, and 905—906).—Alcohols have no action

on Fehling's solution under ordinary conditions, but when they are heated together in sealed tubes at temperatures above  $100^{\circ}$ , the alcohols are oxidised, with formation of the corresponding aldehyde and acid when the alcohol is in excess, and of the corresponding acid only when the Fehling's solution is in excess. Cuprous oxide is precipitated in violet-red octahedra or cubes. In some cases copper also separates in microscopic prisms, terminated by quadratic pyramids.

In the case of ethylic alcohol, if the heating at  $240^{\circ}$ , with excess of Fehling's solution, is prolonged, a small quantity of cupric acetate is formed, and afterwards splits up into cuprous oxide, carbonic anhydride, and acetic acid; with methylic alcohol, a small quantity of cupric formate is formed and decomposes in an analogous manner; with propylic alcohol, small quantities of lactic acid and ethylidene-lactic acid are formed. The reaction  $2[\text{Cu}(\text{C}_3\text{H}_5\text{O}_2)_2] + 2\text{H}_2\text{O} = \text{Cu}_2 + 2\text{C}_3\text{H}_5\text{O}_3 + 2\text{C}_3\text{H}_5\text{COOH}$  is endothermic, and if cupric propionate is heated with water in sealed tubes at  $180\text{--}200^{\circ}$  for 60 hours, small quantities of metallic copper, cuprous oxide, and propionic and lactic acids are formed.

C. H. B.

**Secondary Allylic Alcohols.** By H. FOURNIER (*Bull. Soc. Chim.*, 1894, [3], 11, 359—362).—Several homologues of ethylallylcarbinol have been prepared by the interaction of allylic bromide and zinc with fatty aldehydes (*Abstr.*, 1894, i, 19, 394). They are all colourless liquids of more or less disagreeable odour; the acetates, on the other hand, with the exception of the highest, have agreeable odours. The yield of the alcohols was from 25 to 30 per cent. of the theoretical; that of the acetates about 45 per cent. It is noteworthy that the refractive indices both of the alcohols and of the acetates increase by 0.003 for each increment of  $\text{CH}_2$ , and that the refractive indices of the acetates are uniformly 0.012 less than those of the corresponding alcohols.

*Isopropylallylcarbinol*, from isobutaldehyde, boils at  $139\text{--}141^{\circ}$ ; the sp. gr. at  $15^{\circ}$  is 0.846, the refractive index  $[\alpha]_D = 1.435$ . The *acetate* boils at  $160\text{--}162^{\circ}$ ; the sp. gr. at  $15^{\circ} = 0.891$ , the refractive index  $[\alpha]_D = 1.423$ . *Isobutylallylcarbinol*, from isovaleraldehyde, boils at  $162\text{--}164^{\circ}$ ; the sp. gr. at  $15^{\circ}$  is 0.845, the refractive index  $[\alpha]_D = 1.438$ . The *acetate* boils at  $179\text{--}181^{\circ}$ ; its sp. gr. at  $15^{\circ} = 0.887$ , its refractive index  $[\alpha]_D = 1.426$ . *Hexylallylcarbinol*, from cönanthaldehyde, is slightly viscous, and boils at  $210\text{--}212^{\circ}$ ; the sp. gr. at  $15^{\circ}$  is 0.848, the refractive index  $[\alpha]_D = 1.444$ . The *acetate* boils at  $222\text{--}224^{\circ}$ ; the sp. gr. at  $15^{\circ} = 0.879$ , the refractive index  $[\alpha]_D = 1.432$ .

JN. W.

**Formation of Mannitol in Wines.** By H. and A. MALBOT (*Bull. Soc. Chim.*, 1894, [3], 11, 413—415).—A continuation of previous work (*Abstr.*, 1894, i, 269 and 295). The reduction of glucose may, perhaps, be due to the butyric ferment, which is known to liberate hydrogen, or, possibly, to the propionic ferment.

The presence of an unfermentable, difficultly hydrolysable sugar has been observed in a wine from which all glucose had been removed by fermentation. This sugar was transformed, in the course of some

months, into mannitol, but, in the presence of sulphurous acid, into glucose. JN. W.

**Trehalose in Mushrooms.** By EMILE E. BOURQUELOT (*Bull. Soc. Chim.*, 1894, [3], 11, 353—356).—A claim for priority. The author (Abstr., 1889, 740; 1891, 103) has already obtained the whole of Winterstein's recent results (Abstr., 1894, i, 161). The latter misquotes him in asserting that he stated there is no trehalose in dried mushrooms; his observation was that the trehalose often disappears during the desiccation. JN. W.

**Blue Iodide of Starch and the Molecular Structure of "Dissolved" Starch.** By FRITZ W. KÜSTER (*Annalen*, 1894, 283, 360—379; compare F. Mylius, Abstr., 1887, 568).—Although neither dry nor dissolved starch takes up free iodine in any considerable quantity, the amount of the halogen in blue iodide of starch obtained from either source by treatment with iodine dissolved in potassium iodide, depends closely on the concentration of the solution. The results of numerous experiments lead the author to the conclusion that, contrary to the views of previous investigators, blue iodide of starch is neither a compound nor a mixture, but must be regarded as a well-defined, solid solution of iodine in starch; this confirms the opinion expressed by A. Meyer in a recent monograph.

Regarding its properties from this point of view, "dissolved" starch more closely resembles an emulsion than a solution.

M. O. F.

**The Products of Hydrolysis of Fungus-cellulose.** By ERNST WINTERSTEIN (*Ber.*, 1895, 28, 167—169).—Cellulose prepared from the *Agaraceae* (*Boletus* and *Agaricus*) and from *Helvellaceae* (*Morchella*) has already (this vol., i, 80) been shown to yield glucosamine when heated with hydrochloric acid; this is now shown to be true of cellulose from the *Pezizaceae* (*Botrytis* and *Polyporus*). The same result is obtained if the residue obtained after the fungi have been freed from fat and boiled first with dilute sulphuric acid and then with dilute caustic soda is used, instead of the prepared cellulose.

It is also shown that, just as in the case of chitin, acetic acid is formed in addition to glucosamine; moreover, the above-mentioned residues behave like chitin when fused for an hour with caustic potash at a temperature not exceeding 180°; they yield acetic acid and a substance resembling chitosan. Various species of *Polyporus* furnish, in addition, a cellulose-like substance, insoluble in water, and yielding glucose when hydrolysed. No such product was obtained from *Boletus*, *Agaricus*, or *Morchella*, but the cellulose from the first two yields glucose when hydrolysed, and must therefore contain, in addition to chitin, a substance, possibly a hemicellulose, which yields glucose when hydrolysed, but is destroyed in the potash fusion.

C. F. B.

**Complex Metallic Bases.** By NICOLAI S. KURNAKOFF (*J. pr. Chem.*, 1894, [2], 50, 481—507).—The salient points in this paper have already been published (Abstr., 1894, i, 273).

A. G. B.

**A New Series of Sulphur Derivatives of Aliphatic Amines.**

By AUGUST MICHAELIS and K. LUXEMBOURG (*Ber.*, 1895, **28**, 165—167).

—When sulphur chloride is mixed with secondary amines in cooled ethereal solution, the following reaction occurs:— $S_2Cl_2 + 4NHR_2 = S_2(NR_2)_2 + 2NHR_2.HCl$ . The dithiodiamines formed are decomposed by acids into the amine, sulphur, and sulphurous anhydride. *Dithiodimethylamine*,  $S_2(NMe_2)_2$ , is a reddish-yellow liquid, boiling at  $82-83^\circ$  under 22 mm. pressure, at  $170-180^\circ$ , and with slight decomposition, under atmospheric pressure. *Dithiodiethylamine*,  $S_2(NEt_2)_2$ , is a pale yellow liquid, boiling at  $137-138^\circ$  under 29 mm. pressure, and decomposing when distilled under atmospheric pressure. *Dithiodipiperidine*,  $S_2(C_5NH_{10})_2$ , forms white crystals melting at  $64^\circ$ .

Sulphur chloride also reacts with primary amines, but the products have not yet been carefully studied. C. F. B.

**Choline.** By ERNST SCHMIDT (*Zeit. physiol. Chem.*, 1895, **20**, 364).

—Gulewitsch (this vol., i, 196) finds that Gram's statement concerning the ready conversion of choline into neurine by hydrochloric and lactic acid is incorrect. The present paper shows that the author previously pointed out Gram's error. W. D. H.

**So-called Stereochemistry of Nitrogen.** By ADOLPH CLAUS (*J. pr.*

*Chem.*, 1894, [2], **50**, 567—576).—The author takes exception to the statements which Van't Hoff makes, in the recently published second edition of his book on "*die Lagerung der Atome in Raum*," concerning the isomerism of the oximes. He (the author) has brought forward many instances of oximes which, although fulfilling the conditions laid down by Van't Hoff, do not show isomerism, and devotes this paper to a review of his position. A. G. B.

**Thiosemicarbazide.** By MARTIN FREUND (*Ber.*, 1895, **28**, 306; compare *Ber.*, 1895, **28**, 77).—The melting point of thiosemicarbazide is really  $181-183^\circ$ , and not  $215-218^\circ$ , as previously stated. A. H.

**Polymeric Modifications of Propaldehyde. Parapropaldehyde, and Metapropaldehyde.** By WILLIAM R. ORNDORFF and Miss L. L. BALCOM (*Amer. Chem. J.*, 1894, **16**, 645—650; compare Abstr., 1890, 955; 1894, i, 168).—*Parapropaldehyde*, obtained from pure propaldehyde by the polymerising action of hydrogen chloride, solidifies completely at  $-20^\circ$  to a mass of needle-shaped crystals, and boils at  $169-170^\circ$  (uncorr.), being converted into propaldehyde. It has a sp. gr. of 0.9549 at  $0^\circ/4^\circ$ , is only slightly soluble in water, dissolves readily in ether and in alcohol, and closely resembles paraldehyde in odour and properties. It does not react with hydroxylamine or with a solution of magenta which has been decolorised with sulphurous anhydride, and its molecular weight, as determined by its effect in lowering the melting point of phenol, corresponds with the formula  $C_9H_{18}O_3$  (compare Reformatsky, *J. Russ. Chem. Soc.*, **22**, 197).

The method of preparation of metapropaldehyde has been already described (*loc. cit.*). It closely resembles metaldehyde in its properties, and does not react with hydroxylamine or affect a solution of

magenta decolorised by sulphurous anhydride, and consequently does not contain a COH group. Its molecular weight, determined in the same way as that of paraprovaldehyde, accords also with the formula  $C_9H_{18}O_3$ . On being kept for some time, it appears to be partly converted into a tetraprovaldehyde,  $(C_3H_6O)_4$ .

As neither paraprovaldehyde nor tetraprovaldehyde contains a COH group; as their molecules are of equal weight, and as they both are readily converted into the simple aldehyde by the action of the same reagents, the author suggests that the oxygen atoms play the parts of connecting links, and that the two aldehydes are stereoisomerides. Paraprovaldehyde, being the more stable, is probably the trans-variety, and tetraprovaldehyde the cis-variety.

G. T. M.

**Oxidation of Aliphatic Aldehydes and Ketones by Nitric acid.** By ROBERT BEHREND and HEINRICH TRYLLER (*Annalen*, 1894, **283**, 209—245; compare Abstr., 1893, i, 303, and 1894, i, 108).—Hydroxyisonitrosoacetone nitrite (*loc. cit.*), obtained by oxidising acetone with nitric acid, is to be regarded as *acetylmethylnitrolic acid*,  $COMe \cdot C(NO_2) \cdot NO_2$ ; it crystallises from ether in transparent plates, which melt at 55—62° with evolution of gas. In addition to the products already mentioned (*loc. cit.*), the yellow oil, obtained by the action of nitric acid on acetone, yields pyruvic acid when boiled with water. When the oil is heated, it decomposes and becomes viscous, yielding, on treatment with hydroxylamine hydrochloride, an *oxime*,  $C_6H_8N_4O_4$ , which melts and decomposes at 139—140°; nitric acid converts this substance into a compound of the formula  $C_6H_8N_4O_5$ .

The fact that acetone is acted on by cold nitric acid only when the latter contains nitrous acid, appears to depend on the initial production of isonitrosoacetone, which is then in part converted into acetylmethylnitrolic acid, oxidation occurring at the same time. This explanation is confirmed by the observation that action may be set up in a mixture of acetone and pure nitric acid by introducing a small quantity of isonitrosoacetone; moreover, when mixed with nitric acid of sp. gr. 1.4, isonitrosoacetone is converted into acetylmethylnitrolic acid.

When methyl ethyl ketone is acted on by nitric acid to which a little red fuming acid has been added, formic and acetic acids are formed, together with a small quantity of hydrogen cyanide and ammonia; the other products are ethylnitrolic acid and dinitroethane, the former arising in consequence of the initial formation of isonitroso-methyl ethyl ketone, whilst the latter results from the action of nitric acid on ethylnitrolic acid.

When nitrous acid acts on acetone, acetylmethylnitrolic acid is formed. In the case of methyl ethyl ketone, the products are the isonitroso-derivative and ethylnitrolic acid.

M. O. F.

**Action of Ethylic Chlorocarbonate on the Sodium Derivative of Acetone.** By PAUL C. FREER (*Annalen*, 1894, **283**, 380—391, and *Amer. Chem. J.*, 1895, **17**, 1—18; compare Freer and Higley, Abstr., 1891, 1182).—When ethylic chlorocarbonate acts on sodacetone, a

mixture of sodium chloride and carbonate separates, and a highly refractive oil, which boils at 129—130°, is formed; hydrolysis of this substance with barium hydroxide or with dilute hydrochloric acid gives rise to carbonic anhydride, ethylic and isopropylic alcohols, and acetone. On effecting this decomposition quantitatively, results are obtained, which, in conjunction with analyses and vapour-density determinations, give support to the view that the chief product of the action of ethylic chlorocarbonate on sodacetone is *ethylic isoacetonecarbonate*,  $\text{CH}_3\cdot\text{CMe}\cdot\text{O}\cdot\text{COOEt}$  (*loc. cit.*).

A substance,  $\text{C}_9\text{H}_{14}\text{O}_3$ , is formed at the same time, and can be separated on account of its higher boiling point. It has an odour suggestive of that of mesitylic oxide, and is indifferent towards phenylhydrazine; it boils at 114° under a pressure of 30 mm. The constitution is probably represented by the expression



Ethylic isoacetonecarbonate, when treated with phosphorus pentachloride, yields a mixture of  $\beta$ -chloropropylene and ethylic chlorocarbonate with a small quantity of diethylic carbonate.

M. O. F.

**Ethereal Salts from Active Amylic Alcohol.** By PHILLIPE A. GUYE and L. CHAVANNE (*Compt. rend.*, 1894, 119, 906—909).—The authors have prepared a number of salts from active primary amylic alcohol and the normal acids of the acetic series, and have determined their rotatory powers, with the following results.

	B. p. under 727 mm.	Sp. gr. at 21—24°.	Specific rotatory power $[\alpha]_D$ .	Product of asymmetry $P \times 10^6$ .
Amylic formate...	120—122°	0·882	+2·01	332
„ acetate...	138—139	0·872	+2·53	<b>374</b>
„ propionate	156—158	0·869	+2·77	373
„ butyrate..	173—176	0·862	+2·69	351
„ valerate..	195—197	0·860	+2·52	321
„ caproate..	212—214	0·859	+2·40	289
„ heptylate.	232—235	0·861	+2·21	258
„ caprylate.	250—253	0·860	+2·10	229
„ nonylate..	262—265	0·861	+1·95	204
„ laurate...	305—308	0·859	+1·56	144
„ palmitate.	9·5° m. p.	0·854	+1·45	93·5
„ stearate..	20—21° m. p.	0·855	+1·27	76·7

The value of  $[\alpha]_D$  passes through a maximum corresponding with amylic propionate, whilst the product of asymmetry passes through a maximum corresponding with amylic acetate. The simplified formula adopted by the authors for the product of asymmetry, whilst it indicates the occurrence of a maximum, is not sufficient to exactly determine its position *à priori*.

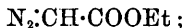
In the preparation of the salts, phosphoric anhydride, as recommended by Young and Thomas (*Trans.*, 1893, 1191), was found to be the only convenient means of removing the excess of amylic alcohol.



Amylic alcohol, obtained by hydrolysing the formate and the palmitate, has the same optical activity as the original alcohol. This fact disposes of (1) the objection of Frankland and Macgregor (*Trans.*, 1893, 1410—1418) that the amylic alcohol employed may be a mixture of two alcohols that etherify at different rates with acids so different in boiling point as formic and palmitic acids, the occurrence of a maximum being then fortuitous; and (2) the objection of Van't Hoff, that partial racemisation may take place during fractional distillation.

C. H. B.

**Ethyllic Mercuridiazooacetate.** By EDUARD BUCHNER (*Ber.*, 1895, 28, 215—221).—This substance,  $\text{Hg}[\text{C}(\text{N}_2)\cdot\text{COOEt}]_2$ , is obtained by dissolving mercuric oxide in cooled ethylic diazoacetate,



it forms yellow, rhombic crystals,  $a : b : c = 0.4546 : 1 : 0.72527$ , and melts and decomposes at  $104^\circ$ . The corresponding *methyllic* salt melts, and decomposes slightly, at  $123^\circ$ . These compounds are slightly explosive and are readily decomposed. The action of water on them has been studied in some detail; at the ordinary temperature it converts the methyllic salt into mercury, nitrogen, methyllic alcohol, oxalic acid, and glycolic acid.

C. F. B.

**Active Amylacetic acid and its Derivatives.** By IDA WELT (*Compt. rend.*, 1894, 119, 855—858).—*Ethyllic amylacetoacetate*, specific rotatory power at  $20^\circ$ ,  $[\alpha]_D = +7.71$ .

*Amylacetic acid*, boiling at  $221^\circ$ , sp. gr. at  $20^\circ = 0.9149$ ; at  $54^\circ = 0.8902$ . Specific rotatory power at  $20^\circ$ ,  $[\alpha]_D = +8.44^\circ$ ; at  $54^\circ$ ,  $[\alpha]_D = +7.64^\circ$ .

*Methyllic amylacetate*, sp. gr. at  $25^\circ = 0.8764$ , and at  $61^\circ = 0.8449$ . Specific rotatory power at  $25^\circ$ ,  $[\alpha]_D = +6.71$ , and at  $75^\circ$ ,  $[\alpha]_D = +5.92$ . *Ethyllic amylacetate*, sp. gr. at  $21^\circ = 0.8644$ , and at  $72^\circ = 0.8250$ . Specific rotatory power at  $21^\circ$ ,  $[\alpha]_D = +6.66$ , and at  $72^\circ$ ,  $[\alpha]_D = +5.87$ .

*Methyl hexyl ketone*,  $\text{COMe}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{11}$ , is obtained by the action of potassium hydroxide on ethylic amylacetoacetate, and boils at  $167$ — $168^\circ$ ; sp. gr. at  $19^\circ = 0.8174$ , and at  $57^\circ$ ,  $0.7893$ ; specific rotatory power at  $21^\circ$ ,  $[\alpha]_D = +5.06$ , and at  $57^\circ$ ,  $[\alpha]_D = +4.41$ . The other optically active products formed at the same time are very viscous liquids, boiling at  $310$ — $330^\circ$  and  $330$ — $370^\circ$  respectively; the latter seems to be mesitylic oxide.

*Methylhexylcarbinol*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{11}$ , obtained by the action of sodium on an alcoholic solution of the ketone, boils at  $167$ — $170^\circ$ ; sp. gr. at  $21^\circ = 0.8174$ , specific rotatory power at  $24^\circ$ ,  $[\alpha]_D = +4.69$ .

In the case of methyllic and ethylic amylacetates, the value of the product of asymmetry, like the rotatory power, decreases, and hence it follows that in this series there is no ethereal salt showing a maximum rotatory power, even the first term being already on the descending branch of the curve. (Compare this vol., ii, 97.)

C. H. B.

**Intramolecular Changes in Unsaturated Acids.** By RUDOLPH FITTIG (*Annalen*, 1894, **283**, 47—65; compare Abstr., 1893, i, 189).—This paper embodies the experimental results described in the following communications. As already stated (*loc. cit.*),  $\beta\gamma$ -unsaturated acids are changed by boiling aqueous soda into the isomeric  $\alpha\beta$ -acids, which, unlike the former, are not converted into lactones by dilute sulphuric acid; this difference in behaviour affords a ready means of separating the isomerides. The method, however, is not applicable to aromatic unsaturated acids, owing to the formation of acid bye-products during the conversion of the  $\beta\gamma$ -acids into the isomeric lactones; moreover, the  $\alpha\beta$ -acids yield lactones under the influence of dilute sulphuric acid.

The conversion of  $\beta\gamma$ -unsaturated acids into the  $\alpha\beta$ -isomerides is attended with the formation of  $\beta$ -hydroxy acids; the  $\gamma$ -hydroxy-acids are never formed, nor can they be obtained by the action of boiling aqueous soda on the  $\beta$ -acid. The production of a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated acids when the  $\beta$ -hydroxy-acids are treated with soda, finds a parallel in the behaviour of the  $\beta$ -bromo-acids. These, in general, are converted by boiling water into a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated acids, with a preponderating amount of  $\beta$ -hydroxy-acid; in the case of phenyl- $\beta$ -bromovaleric acid, however, the  $\beta\gamma$ -acid is not formed.  
M. O. F.

**Intramolecular Change in  $\beta\gamma$ -Pentenic (Ethylidenepropionic) acid. Experiments with  $\gamma\delta$ -Pentenic acid.** By RUDOLPH FITTIG and JOHN G. SPENZER (*Annalen*, 1894, **283**, 66—79 and 79—81).—When the sodium salt of  $\beta\gamma$ -pentenic acid is boiled in aqueous solution with 10 per cent. soda (9 mols.) for 10—20 hours in a copper flask, it is converted into sodium propylideneacetate (compare Ott, Abstr., 1891, 1453). The barium salt contains  $4\text{H}_2\text{O}$ , losing  $2\text{H}_2\text{O}$  with great readiness; the calcium salt, with  $4\text{H}_2\text{O}$ , forms flat, nacreous prisms. Bromine converts the acid into  $\alpha\beta$ -dibromovaleric acid,  $\beta$ -bromovaleric acid being formed by the action of hydrogen bromide.

$\beta$ -Hydroxyvaleric acid is produced during the conversion of ethylidenepropionic into propylideneacetic acid. It is a colourless syrup which remains liquid at  $-18^\circ$ . The calcium salt contains  $1\text{H}_2\text{O}$ ; it becomes anhydrous at  $175^\circ$ , and melts at  $180^\circ$ . The barium salt forms monosymmetric plates which contain  $1\text{H}_2\text{O}$  and melt at  $105^\circ$ ; the silver salt is also crystalline. When the aqueous solution of the acid is boiled for 30 hours with soda, rather more than one half is unattacked; the remainder, however, is converted into a mixture of ethylidenepropionic and propylideneacetic acids. These acids are also produced when  $\beta$ -hydroxyvaleric acid is submitted to dry distillation.

Allylmalonic and allylacetic acids are quite indifferent towards alkali.  
M. O. F.

**Pentenic Acids from the Interaction of Propaldehyde and Malonic acid.** By RUDOLPH FITTIG and JOHN E. MACKENZIE (*Annalen*, 1894, **283**, 82—100; compare preceding abstract, and

A. Viefhaus, Abstr., 1893, i, 392).—The conclusion arrived at by Viefhaus (*loc. cit.*), respecting the composition of the acid mixture obtained by heating propaldehyde with malonic and acetic acids, is confirmed.

Boiling water converts  $\beta$ -bromovaleric acid into a mixture of  $\beta$ -hydroxyvaleric acid (56 per cent.), propylideneacetic (11 per cent.), and ethylidenepropionic (10 per cent.) acids; a small quantity of butylene is also produced.

Ethylidenepropionic acid yields  $\beta\gamma$ -dibromovaleric acid when acted on by bromine; this crystallises in transparent prisms which melt at  $65-65.5^\circ$  (compare Fittig and Fränkel, Abstr., 1890, 585). Hydrogen bromide converts it into a mixture of  $\beta$ - and  $\gamma$ -bromovaleric acids, which, when boiled with water, yields ethylidenepropionic, propylideneacetic, and  $\beta$ -hydroxyvaleric acids, mixed with valerolactone (50 per cent.).

M. O. F.

**Crystalline Form of Bromo- and Dibromo-valeric acids.** By RUDOLPH FITTIG (*Annalen*, 1894, 283, 100—104).— $\beta$ -Bromovaleric acid forms monosymmetric crystals;  $a : b : c = 1.4688 : 1 : 0.4900$ .  $\beta = 79^\circ 58' 45''$ .

$\alpha\beta$ -,  $\beta\gamma$ -, and  $\gamma\delta$ -dibromovaleric acids also form crystals belonging to the monosymmetric system, and having the following ratios respectively.

$$a : b : c = 1.2016 : 1 : 0.4808. \quad \beta = 88^\circ 48'$$

$$a : b : c = 0.9509 : 1 : 0.8781. \quad \beta = 82^\circ 20'$$

$$a : b : c = 5.5159 : 1 : \quad ? \quad \beta = 77^\circ 10'$$

M. O. F.

**Intramolecular Change in Angelic and Tiglic acids.** By RUDOLPH FITTIG (*Annalen*, 1894, 283, 105—109).—The separation of angelic and tiglic acids by means of the calcium salts is almost quantitative; it is therefore possible to study their behaviour towards boiling aqueous soda.

When angelic acid (10 grams) is heated with soda (40 grams), dissolved in water (160 grams) for 20 hours in a reflux apparatus, tiglic acid (6.3 grams) is formed. The yield is influenced by the temperature maintained, and therefore depends on the concentration of the alkali employed. Thus, when angelic acid is heated with water (15 parts) for 20 hours at  $120^\circ$ , one-half its weight of tiglic acid is produced.

Tiglic acid undergoes no change when heated for 20 hours with a 20 per cent. solution of soda.

M. O. F.

**Oxidation of Tiglic and Angelic acids.** By RUDOLPH FITTIG and MAX PENSCHUCK (*Annalen*, 1894, 283, 109—117; compare I. Kondakoff, Abstr., 1892, 1304).—*Tigliceric acid*,  $C_8H_8(OH)_2O_2$ , is obtained by the oxidation of tiglic acid in alkaline solution with potassium permanganate. It melts at  $88^\circ$ , and forms crystals belonging to the monosymmetric system;  $a : b : c = 1.0665 : 1 : 0.7903$ .  $\beta = 73^\circ 26'$ . The barium, calcium, and silver salts are very soluble in water; the zinc salt dissolves more readily in cold water than in hot.

*Angliceric acid* is obtained in a similar manner from angelic acid;

it melts at 110—111°. The *calcium* and *zinc* salts are readily soluble in water.

Neither of these acids yields a hydroxy-lactone under the influence of hydrochloric acid. M. O. F.

### Intramolecular Change in $\beta\gamma$ -Hexenic (Hydrosorbic) acid.

By RUDOLPH FITTIG and CHARLES F. BAKER (*Annalen*, 1894, **283**, 117—128).— $\alpha\beta$ -Hexenic acid,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$ , is formed when hydrosorbic acid is heated with a 20 per cent. solution of soda for 20—50 hours. It melts at 32·7—33·1°, and boils at 216—217°. The *calcium* salt, with  $3\text{H}_2\text{O}$ , forms white plates; the *barium* salt contains  $1\frac{1}{2}\text{H}_2\text{O}$ . The *silver* salt forms white needles, the *cadmium* salt contains  $2\text{H}_2\text{O}$ , and the *zinc* salt with  $2\frac{1}{2}\text{H}_2\text{O}$  crystallises in silky needles. Bromine converts the acid into  $\alpha\beta$ -dibromocaproic acid, which melts at 70·5—71·5°, and differs from the isomeric obtained from sorbic acid and hydrogen bromide.  $\beta$ -Bromocaproic acid is obtained by the action of hydrogen bromide on  $\alpha\beta$ -hexenic acid; it is insoluble in water, and melts at 34·5—35°. When boiled for two hours with water, carbonic anhydride is eliminated, and a small quantity of amylene is formed; rather more than half the acid, however, is converted into  $\beta$ -hydroxycaproic acid, a colourless syrup which dissolves readily in water, and is not volatile in a current of steam. The *barium* salt crystallises in white plates containing  $1\text{H}_2\text{O}$ , and the *calcium* salt contains  $\frac{1}{2}\text{H}_2\text{O}$ ; the *silver* salt forms white needles.

$\alpha\beta$ -Hexenic acid yields about one-fourth of its weight of  $\beta$ -hydroxycaproic acid when boiled with 10 per cent. aqueous soda, the remainder undergoing no change. This action is reversible,  $\beta$ -hydroxycaproic acid yielding 30 per cent. of  $\alpha\beta$ -hexenic acid when treated with boiling aqueous soda. M. O. F.

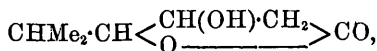
### Intramolecular Change in $\beta\gamma$ -Isoheptenic acid.

By RUDOLPH FITTIG and JULIUS FEURER (*Annalen*, 1894, **283**, 129—148).— $\alpha\beta$ -Isoheptenic acid,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$ , is obtained by heating  $\beta\gamma$ -isoheptenic acid with 10 per cent. aqueous soda for 30 hours; it melts at 16·5°, and boils at 227—228°. The *calcium* salt with  $4\text{H}_2\text{O}$  forms characteristic aggregates of needles; the *barium* salt resembles it, and contains  $7\frac{1}{2}\text{H}_2\text{O}$ . The *silver* salt crystallises in lustrous plates, and is not altered by light.  $\alpha\beta$ -Dibromischoheptic acid, which melts at 116—117°, forms crystals belonging to the monosymmetric system;  $a:b:c = 0\cdot732:1:0\cdot641$ .  $\beta = 58^\circ 0' 9''$ .  $\beta$ -Bromischoheptic acid is obtained by the action of hydrogen bromide on  $\alpha\beta$ -isoheptenic acid; it melts at 26—27°, and dissolves very readily in organic solvents. Boiling water converts it into a mixture of hexylene,  $\alpha\beta$ - and  $\beta\gamma$ -isoheptenic acids, and  $\beta$ -hydroxyischoheptic acid, the latter being also obtained by the action of boiling aqueous soda on  $\beta\gamma$ -isoheptenic acid; it forms small, lustrous plates, and melts at 64·5°. The *barium* salt contains  $2\text{H}_2\text{O}$ , and the *calcium* salt  $1\frac{1}{2}\text{H}_2\text{O}$ ; the *silver* salt is indifferent towards light. When  $\beta$ -hydroxyischoheptic acid is submitted to dry distillation, nearly one-half passes over unchanged, whilst the remainder is converted into  $\alpha\beta$ -isoheptenic acid with a small quantity of the  $\beta\gamma$ -acid. These

acids are also formed when the hydroxy-acid is heated with 10 per cent. aqueous soda for 30 hours, 75 per cent. remaining unaltered.

Boiling aqueous soda converts  $\alpha\beta$ -isoeptenic acid into a mixture of  $\beta$ -hydroxyheptoic and  $\beta\gamma$ -isoeptenic acids. M. O. F.

**Oxidation Products of  $\beta\gamma$ - and  $\alpha\beta$ -Isoeptenic acids.** By RUDOLPH FITTIG and ALFRED SILBERSTEIN (*Annalen*, 1894, **283**, 269—279).—*Hydroxyisoeptolactone*,



is obtained by oxidising  $\beta\gamma$ -isoeptenic acid with potassium permanganate. It melts at  $112^\circ$ , and forms crystals belonging to the monosymmetric system;  $a : b : c = 2.1494 : 1 : 1.2600$ .  $\beta = 78^\circ 3'$ . When the lactone is heated with hot aqueous barium hydroxide, the barium salt of  $\beta\gamma$ -dihydroxyheptoic acid is formed; the calcium salt contains  $1\text{H}_2\text{O}$ , and the silver salt rapidly darkens on exposure to light.

*Isoeptenolactone*,  $\text{CHMe}_2\cdot\text{C}\left\langle\underset{\text{O}}{\text{CH}\cdot\text{CH}_2}\right\rangle\text{CO}$ , is formed on distilling hydroxyisoeptolactone; it is a colourless oil which boils at  $225\text{--}230^\circ$ .

$\delta$ -Dimethyllevulinic acid,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , is obtained by the action of hot aqueous alkalis on isoeptenolactone; it crystallises in long needles, and melts at  $41^\circ$ . The barium salt is anhydrous.

$\alpha\beta$ -Dihydroxyisoeptoic acid,



is obtained by oxidising  $\alpha\beta$ -isoeptenic acid. It crystallises in small needles, and melts at  $114^\circ$ . The calcium salt contains  $3\text{H}_2\text{O}$ , and the barium salt  $1\text{H}_2\text{O}$ ; the silver salt slowly becomes coloured when exposed to light. The acid does not form a lactone, and remains unchanged when heated with 10 per cent. aqueous soda for 20 hours, resembling, in this respect, the  $\beta\gamma$ -isomeride. M. O. F.

**Intramolecular Change in  $\beta\gamma$ -Isoctenic acid.** By RUDOLPH FITTIG and SYLVIAN WEIL (*Annalen*, 1894, **283**, 279—291).—The anhydride of isobutylcitraconic acid is produced on distilling isobutylparaconic acid; the acid itself,  $\text{C}_9\text{H}_{14}\text{O}_4$ , melts at  $75\text{--}80^\circ$ , and forms a barium salt which is more soluble in cold water than in hot.

$\beta\gamma$ -Isoctenic acid is also formed when isobutylparaconic acid is distilled, and on treatment with a hot, 10 per cent. solution of soda for 30 hours, it is converted into  $\alpha\beta$ -isocenic acid, which melts at  $3^\circ$  and boils at  $239\text{--}240^\circ$ ; this action is reversible. The calcium salt contains  $1\text{H}_2\text{O}$ , and the barium salt is anhydrous; the silver salt becomes yellow on exposure to light.

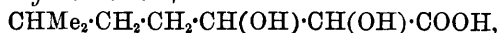
$\alpha\beta$ -Dibromisocetoic acid crystallises in needles which melt at  $58\text{--}59^\circ$ .  $\beta$ -Bromisocetoic acid is obtained by the action of hydrogen bromide on  $\alpha\beta$ -isocenic acid. It is a yellowish oil, and when boiled with water yields a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -isocenic acids with  $\beta$ -hydroxyisocetoic acid, which is also obtained by heating  $\beta\gamma$ -isocenic

acid with aqueous soda. It crystallises in silky needles, and melts at 36—37°. The *barium* and *calcium* salts contain 1H<sub>2</sub>O; the *silver* salt is not changed by exposure to light. M. O. F.

**Oxidation Products of  $\beta\gamma$ - and  $\alpha\beta$ -Isoctenic acids.** By RUDOLPH FITTIG and FRANÇOIS DE VOS (*Annalen*, 1894, **283**, 291—297).—*Hydroxyisocetolactone*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}<\text{O}-\text{CH}(\text{OH})\cdot\text{CH}_2>\text{CO}$ , is

produced when  $\beta\gamma$ -isocetenic acid is oxidised with potassium permanganate; it crystallises in needles, and melts at 33—34°. Hot aqueous alkalis convert the lactone into salts of  $\beta\gamma$ -dihydroxyisocetonic acid; the *barium* and *calcium* salts are crystalline, and do not contain water; the *silver* salt is also crystalline. When the lactone is distilled, an unsaturated lactone is formed, and this is converted by alkalis into *isopropyllevulinic acid*, which crystallises in colourless needles, and melts at 47°. The *barium* salt is anhydrous, and the *calcium* salt contains 3H<sub>2</sub>O; the *silver* salt forms colourless crystals.

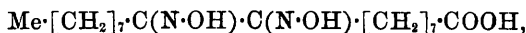
*$\alpha\beta$ -Dihydroxyisocetonic acid,*



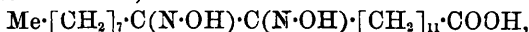
is obtained by oxidising  $\alpha\beta$ -isocetenic acid with potassium permanganate; it does not give rise to a lactone, and is quite indifferent towards 10 per cent. aqueous soda. The *barium* and *calcium* salts are anhydrous; the *silver* salt crystallises from hot water.

M. O. F.

**Stearoxylic acid and Behenoxylic acid.** By A. SPIECKERMANN (*Ber.*, 1895, **28**, 276—279).—Stearoxylic acid reacts with hydroxylamine to form *diketoxime stearic acid*,



which crystallises in white, microscopic needles, melting at 153—154°. *Diketoxime behenic acid*,



is obtained in a similar manner from behenoxylic acid, and crystallises in matted, white needles which melt at 144—145°. When only about 1 mol. of hydroxylamine is used, the ketoximebehenic acid is accompanied by behenic acid and *ketoximeketobehenic acid*, which forms microscopic needles melting indefinitely at 83—88°.

Stearoxylic acid is therefore 9 : 10-diketostearic acid, whilst behenoxylic acid is 13 : 14-diketobehenic acid. A. H.

**Electrosyntheses by the Direct Union of Anions of Weak Organic Acids.** By J. B. WEEMS (*Amer. Chem. J.*, 1894, **16**, 569—588).—The author has investigated the behaviour of such oxidising agents as hydrogen peroxide, potassium permanganate, and chromic acid on ethylic malonate, ethylic methanetricarboxylate, and acetylacetone, and finds that the same products are not obtained as when those substances are electrolysed. The formation of the new compounds by electrolysis is best explained as the result of the direct union of the anions. This union takes place very readily during the electrolysis of sodium compounds of derivatives of ethylic malonate. Ethylic dimethylethanetetracarboxylate and diethylethanetetracarboxylate

oxylate are thus obtained from ethylic methylmalonate and ethylmalonate, but in yield smaller than from ethylic malonate and ethylic methanetricarboxylate. No evidence of a pairing of anions was obtained during the electrolysis of ethylic benzoylmalonate and acetylmalonate. Compounds such as ethylic acetoacetate and slightly impure acetylacetone gave, on electrolysis, distinct evidence of the pairing of anions, but no such synthetical products were obtained from ethylic acetonedicarboxylate and acetylbenzoylmethane, and the reaction must not therefore be regarded as a typical one. The formation of bis-phenylmethylpyrazalone in the electrolysis of phenylmethylpyrazalone may be partly an electrolysis of this type, or may be due entirely to oxidation.

The electrolysis of acid amides, such as acetamide, benzamide, succinimide, and phthalimide, or of their sodium or mercury derivatives, yields the original amides or imides without any pairing of anions.

G. T. M.

**Trimethylsuccinic acid and the Symmetrical Dimethylglutaric acids.** By KARL AUWERS (*Ber.*, 1895, 28, 263—270).—According to Zelinsky (*Abstr.*, 1891, 669), two isomeric trimethylsuccinic acids are formed by the hydrolysis of the product of the action of ethylic  $\alpha$ -bromisobutyrate on ethylic  $\alpha$ -cyanopropionate. Since the accepted stereochemical theory only admits the possibility of one acid of this constitution, and as the statements of different investigators with regard to these acids are not in complete agreement, the author has reinvestigated the matter. He has found that trimethylsuccinic acid only exists in one form, and that symmetrical dimethylglutaric acid exists in two stereoisomeric forms. The acid usually described as symmetrical dimethylglutaric acid, and that supposed by Zelinsky to be a second trimethylsuccinic acid, are both mixtures of the two isomeric dimethylglutaric acids.

Trimethylsuccinic acid was prepared by Zelinsky's method, by the oxidation of camphoric acid (*Abstr.*, 1894, i, 46), by the dry distillation of camphoronic acid (*Abstr.*, 1894, i, 141; Helle, *Inaug. Diss.*, Bonn, 1893, 21), and by the action of ethylic  $\alpha$ -bromisobutyrate on ethylic sodiomethylmalonate in solution in xylene and in alcohol (*Abstr.*, 1891, 828; Helle). The pure acid obtained by each of these methods melts at 147—148°, but the melting point varies a little with the rate at which the acid is heated. The numbers given by previous investigators vary from 131° to 141°. At 152—153° the acid loses water and forms the anhydride, which boils at 227° and melts at 31°; 100 parts of water dissolve 9.57 of the acid at 15°. The electrical conductivity  $k = 0.0304$ . The barium and zinc salts are crystalline. The following derivatives have been prepared. The *anilic acid*, melting at 134—135°, the *anil*, melting at 129°, the *paratolil*, melting at 117°, and the  $\beta$ -*naphthil*, of melting point 148°, crystallise in needles, whilst the *paratolilic acid*, which melts at 126°, forms tablets, and the  $\beta$ -*naphthilic acid*, melting at 153°, crystallises in prisms.

Symmetrical dimethylglutaric acid obtained from ethylic sodio- $\alpha$ -cyanopropionate and methylenic iodide (*Abstr.*, 1890, 132) from the

latter and ethylic sodiomethylmalonate (Abstr., 1890, 1099) from ethylic  $\alpha$ -bromisobutyrate and ethylic sodiomethylmalonate (Abstr., 1890, 743, 1098; 1891, 1015; 1894, i, 72), and by the methylation of ethylic dicarboxyglutarate (Abstr., 1891, 178) is a mixture in nearly equal proportions of two stereoisomeric acids. The acid obtained by Zelinsky, and supposed by him to be a new trimethylsuccinic acid, on the other hand, contains much more of the maleinoid than of the fumaroid acid. The two can readily be separated by means of the calcium salts, or by the action of acetic chloride.

The *fumaroid acid*, which has not previously been described, crystallises from hot water in compact flat monosymmetric needles melting at  $140-141^{\circ}$ . One hundred parts of water dissolve 4.4 of the acid at  $17^{\circ}$ ; 5.6 at  $25^{\circ}$ . The acid is not volatile with steam, even from solutions made strongly acid with sulphuric acid, has an electrical conductivity  $k = 0.00593$ , and is optically inactive. It may be distilled under reduced pressure without undergoing any change, and small quantities may be distilled under the ordinary pressure, but when slowly distilled in the air, it loses water, and forms the *anhydride* melting at  $94-95^{\circ}$ , which is given by both of the acids. Hydrochloric acid at  $190-200^{\circ}$  partially transforms the acid into the stereoisomeric form, a mixture of about equal parts of the two forms being produced. Boiling acetic chloride is without action, but at  $100^{\circ}$  produces the anhydride mentioned above.

The acid melting at  $127-128^{\circ}$ , which has been described by Zelinsky, is the maleinoid form; 100 parts of water dissolve 4.1 of the acid at  $15^{\circ}$ ; 4.9 at  $25^{\circ}$ . When distilled at a low pressure, the acid is not decomposed, but is partially converted into the isomeride; at 200 mm. it is largely converted into the anhydride. Acetic chloride converts it in the cold into the anhydride, whilst hydrochloric acid at a high temperature partially converts it into the isomeride. The anhydride boils at  $272^{\circ}$ , and solidifies to monosymmetric crystals. The *imide* obtained from both of the acids crystallises in needles melting at  $173-174^{\circ}$ . The *anilic acid*, melting at  $157^{\circ}$ ; the *anil*, at  $208-209^{\circ}$ ; the *paratolilic acid*, at  $179^{\circ}$ ; the *paratolil*, at  $233^{\circ}$ ; the  $\beta$ -*naphthil*, at  $231-232^{\circ}$ ; and the  $\alpha$ -*naphthilic acid*, at  $155^{\circ}$ , all crystallise in needles, whilst the  $\beta$ -*naphthilic acid* forms flat prisms melting at  $151^{\circ}$ , and the  $\alpha$ -*naphthil* crystallises in plates melting at  $199^{\circ}$ . A mixture of equal parts of these two acids melts at  $104.5^{\circ}$ , and has been hitherto mistaken for a single acid (Zelinsky, Bischoff, Auwers); 100 parts of water dissolve 8.5 of the mixed acids at  $17^{\circ}$ . As already mentioned, the acid melting at  $100-101^{\circ}$ , which was described by Zelinsky as trimethylsuccinic acid, is a mixture of the two dimethylglutaric acids, the maleinoid form being present in greater proportion.

A. H.

**Secondary Ethereal Acidyltartrates.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1894, [3], 11, 366-374).—With two exceptions, these are all liquids, and have somewhat lower boiling points than the corresponding normal compounds (compare this vol., i, 174).

*Isopropyllic diacetyltartrate* crystallises in prisms, and melts at  $33^{\circ}$ ;



the rotatory power in alcoholic solution at  $20^{\circ}$  is  $[\alpha]_D = +5.9^{\circ}$ . The *isobutylic* salt boils under 12 mm. pressure at  $196-197^{\circ}$ ; the sp. gr. = 1.096 at  $16.5^{\circ}$ . The sp. rotatory power of the liquid at  $18.5^{\circ}$  is  $[\alpha]_D = +17^{\circ}$ ; of the alcoholic solution,  $[\alpha]_D = +11.8^{\circ}$ .

*Isobutylic dipropionyltartrate* boils under 15 mm. pressure at  $207-208^{\circ}$ ; the sp. gr. = 1.073 at  $16.5^{\circ}$ . The sp. rotatory power at  $19^{\circ}$  of the liquid is  $[\alpha]_D = +11.4^{\circ}$ ; of the alcoholic solution,  $[\alpha]_D = +10.2^{\circ}$ . The *dibutyryltartrate* boils under 20 mm. pressure at  $221-223^{\circ}$ ; the sp. gr. = 1.050 at  $16^{\circ}$ . The sp. rotatory power at  $19^{\circ}$  of the liquid is  $[\alpha]_D = +8.5^{\circ}$ ; of the alcoholic solution,  $[\alpha]_D = +8.1^{\circ}$ . The *divaleryl tartrate* decomposes when boiled; the sp. gr. = 1.032 at  $18.5^{\circ}$ ; the sp. rotatory power of the liquid is  $[\alpha]_D = +7.4^{\circ}$ ; of the alcoholic solution,  $[\alpha]_D = +7.7^{\circ}$ . The *dicaproyltartrate* has a sp. gr. = 1.013 at  $13^{\circ}$ . The sp. rotatory power at  $16^{\circ}$  is  $[\alpha]_D = +6.0^{\circ}$ , that of the alcoholic solution,  $[\alpha]_D = +5.5^{\circ}$ .

*Methylic diisobutyryltartrate* crystallises in prisms, and melts at  $45^{\circ}$ ; the sp. rotatory power of the alcoholic solution at  $17^{\circ}$  is  $[\alpha]_D = -13.4^{\circ}$ . The *ethylic* salt has a sp. gr. = 1.095 at  $17^{\circ}$ . The sp. rotatory power at  $17.5^{\circ}$  is  $[\alpha]_D = -1.5^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +1.4^{\circ}$ . The *propylic* salt has a sp. gr. = 1.066 at  $16^{\circ}$ . The sp. rotatory power at  $18^{\circ}$  is  $[\alpha]_D = +2.2^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +4.7^{\circ}$ . The *isobutylic* salt has a sp. gr. = 1.048 at  $16.5^{\circ}$ . The sp. rotatory power at  $14^{\circ}$  is  $[\alpha]_D = +8.4^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +10.1^{\circ}$ .

*Methylic diisovaleryl tartrate* is a liquid of sp. gr. 1.107 at  $16.5^{\circ}$ ; the sp. rotatory power at  $14.5^{\circ}$  is  $-13.9^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = -9.4^{\circ}$ . The *ethylic* salt has a sp. gr. = 1.067 at  $17.5^{\circ}$ . The sp. rotatory power at  $16^{\circ}$  is  $[\alpha]_D = -1.4^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +0.5^{\circ}$ . The *propylic* salt has a sp. gr. = 1.049 at  $18.5^{\circ}$ . The sp. rotatory power at  $16^{\circ}$  is  $[\alpha]_D = +0.7^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +1.7^{\circ}$ . The *isobutylic* salt has a sp. gr. = 1.028 at  $18^{\circ}$ . The sp. rotatory power at  $16^{\circ}$  is  $[\alpha]_D = +5.7^{\circ}$ ; that of the alcoholic solution,  $[\alpha]_D = +6.0^{\circ}$ .

The specific rotatory powers thus vary much in the same sense as those of the corresponding normal compounds; alcohol, however, has a depressing effect in the first terms of the isobutylic series. Propyl has greater weight than isopropyl, whilst the opposite is the case with the butyls and butyryls, as already observed by Frankland and Macgregor in the case of the glycerates.

The author calculates the moments of the substituted chains by a modification of Guye's method, assuming that the bond between two singly-linked carbon tetrahedra is perfectly mobile; the figures obtained for propyl and isopropyl are in the ratio of 159 to 146, thus according in sense with the specific rotatory powers, but those calculated for butyl (or butyryl) and isobutyl (or isobutyryl) are in the ratio of 473 to 460, and are directly opposed in sense to the experimental results.

JN. W.

**Action of Sodium on Ethylic Aconitate and Citrate.** By PAUL C. FREER (*Amer. Chem. J.*, 1895, 17, 31-33).—Sodium and sodium ethoxide both act on each of these salts, with evolution of hydrogen.

With the aconitate, two sodium derivatives appear to be formed, of which one has probably the formula  $C_{22}H_{26}O_{11}Na_4$ . With dilute sulphuric acid, both sodium compounds yield a ketone of the formula  $C_9H_{12}O_6$ , which forms a non-crystallisable compound with phenylhydrazine. The derivative from ethylic citrate appears to be similar in character. These reactions are similar to those obtained by Dieckmann (Abstr., 1894, i, 172 and 324) from tiglic and pimelic acids, and are being further studied.

L. T. T.

**Allofurfurylacrylic acid.** By CARL T. LIEBERMANN (*Ber.*, 1895, 28, 129—134; compare Abstr., 1894, i, 173).—The substance hitherto described as allofurfurylacrylic acid, melting indefinitely at 83—87°, still contains a small amount of furfurylacrylic acid melting at 141°. This can be removed by converting the allo-acid into its piperidine salt, and recrystallising this from benzene, in which the salt of the allo-acid is much less soluble than that of furfurylacrylic acid itself. The recrystallised salt, on decomposition, yields an allo-acid which is free from furfurylacrylic acid and melts at 103—104° quite sharply. The mother liquors from the allo-salt were found to contain small, but quite recognisable amounts of furfurylacrylic acid. The pure acid is not so readily converted into the isomeric form by heating with benzene as the impure form which has hitherto been described. The separation of the small amount of furfurylacrylic acid from the allo-acid melting at 83—87° cannot be effected by direct recrystallisation.

The heat of combustion of the impure allo-acid (m. p. 82—86°) is 761.6 Cal., and its electrolytical conductivity (100 K) 0.00782, the corresponding constants for furfurylacrylic acid being 757.3 Cal. and 0.00325.

A. H.

**Derivatives of Unsymmetrical Tribromobenzene.** By C. LORING JACKSON and F. B. GALLIVAN (*Ber.*, 1895, 28, 190—191).—Tribromodinitrobenzene (m. p. 135°), when reduced with zinc and hydrochloric acid, yields a bromophenylenediamine (m. p. 95°), which gives a tetrabromo-derivative melting at 214°; both these substances have been previously prepared from dinitrotetrabromobenzene [ $(NO_2)_2 = 1:3$ ], and therefore the original tribromodinitrobenzene has the constitution usually assigned to it, namely [ $(NO_2)_2:Br_3 = 1:3:2:4:5$ ]. With sodium ethoxide the compound yields a tribromodiethoxybenzene, melting at 158°. *Bromodinitrodianilidobenzene* melts at 191—192°. Tribromonitrobenzene [ $NO_2:Br_3 = 1:3:4:5$ ], on reduction, yields *tribromaniline*, which melts at 80°, and yields tetrabromobenzene (m. p. 174—175°), showing that the commonly accepted constitution for the latter compound is correct.

J. B. T.

**Reduction of Orthonitrobenzonitrile.** By JOHANNES PINNOW and FRICH MÜLLER (*Ber.*, 1895, 28, 149—160).—1:2-Nitrobenzonitrile,  $NO_2 \cdot C_6H_4 \cdot CN$ , was prepared from orthonitraniline by Sandmeyer's reaction; with hydroxylamine hydrochloride and alcoholic sodium methoxide, it yields a colourless *amidoxime*,  $NO_2 \cdot C_6H_4 \cdot C(NH_2):NOH$ , melting at 146° (uncorr.). When reduced with tin and hydrochloric acid at the ordinary temperature, it yields 1:2-*amidobenzonitrile*,  $NH_2 \cdot C_6H_4 \cdot CN$ ,

together with some amidobenzamide; the amidonitrile melts at 46—47°, and boils at 264—266° under 760 mm. pressure; it is itself unstable in air, but its *hydrochloride* is stable. The substance described by Hübner and Baerthlein (Abstr., 1878, 140) as ortho-amidobenzonitrile, was in reality a mixture of that substance with orthoamidobenzamide.

When 1 : 2-nitrobenzonitrile is heated with methyl-alcoholic soda, it is converted into 1 : 2-methoxybenzamide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CONH}_2$ ; this melts at 128—129°, and was found to be identical with the amide prepared from 1 : 2-methoxybenzoic acid. The *chloride* of this acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , is a liquid boiling at 254° under 760 mm. pressure.

When 1 : 2-nitrobenzonitrile is boiled with very dilute (2 per cent.) hydrochloric acid, and tin gradually added, it is reduced to 1 : 2-azoxybenzonitrile,  $\text{O} < \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CN} \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CN} \end{smallmatrix}$ ; this crystallises in red needles, and melts at 194—195°; it is hydrolysed by strong hydrochloric acid at 180—190° to 1 : 2-azoxybenzimidazole,  $\text{O} < \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \end{smallmatrix} > \text{NH}$ , which crystallises in brown prisms, and does not melt below 320°.

When 1 : 2-nitrobenzonitrile is reduced at 30° with dilute acetic acid and zinc dust, 1 : 2-amidobenzamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CONH}_2$ , is formed (its *stannochloride* melts at 174°), and also some 1 : 2-azoxybenzonitrile, together with a basic substance that appears to have the formula  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{C}(\text{NH}_2) \cdot \text{N} : \text{C} \\ \text{N} \text{-----} \text{N} \end{smallmatrix} > \text{C}_6\text{H}_4$ , and, if so, is *diphenyleneamido-pyrodiazoline*. This substance and its *hydrochloride* crystallise in yellow needles, and melt respectively at 221° and 277°; it yields yellow *monacetyl* and *monobenzoyl derivatives*, melting at 269—270° and 255—256° respectively. When it is hydrolysed with strong hydrochloric acid at 180°, a substance,  $\text{C}_{14}\text{H}_9\text{N}_3\text{O}$ , is formed; this crystallises in yellow prisms, begins to sublime at 320°, and has the properties of a phenol (its yellow *methylic ether* melts at 214°); the hydrolysis has doubtless effected the displacement of  $\text{NH}_2$  by  $\text{OH}$ . If the phenolic substance is nitrated, or even if it is treated with nitrous acid, a  $\text{NO}_2$  group is introduced, and a substance,  $\text{C}_{14}\text{H}_9\text{N}_3\text{O}_3$ , is obtained, which crystallises in yellow needles, and does not melt below 320°. The same product is obtained if the original base, or its acetyl derivative, is treated in boiling acetic acid solution with sodium nitrite; the introduction of a  $\text{NO}_2$  group, and displacement of  $\text{NH}_2$  by  $\text{OH}$ , must thus take place simultaneously in this reaction.

The melting and boiling points given above are uncorrected.

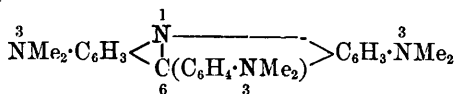
C. F. B.

**Action of Nitrosodimethylaniline on Tertiary and Secondary Aromatic Amines in presence of Concentrated Hydrochloric acid (and Formaldehyde).** By RICHARD MÖHLAU and ARTHUR NEUBERT (*Ber.*, 1895, 28, 324—327).—The compounds previously termed hexamethyltriamidophenylacridine and octomethyltetramidophenylacridine (Abstr., 1893, i, 470) prove to be *biparadimethylamido-benzylideneparaphenylenediamine*,

$$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2,$$
 and *paradimethylamidobenzylideneparamidodimethylaniline*,  

$$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$$

(compare F. Bender, this vol., i, 109). For purposes of comparison the compound



was prepared from dimethylparamidobenzaldehyde and metamido-dimethylaniline; it differs from the "hexamethylene" compound in the greenish-yellow fluorescence of its solutions, the stability and ready solubility of its yellow salts, and the production of a leuco-derivative when reduced. The paper concludes with an account of the changes in colour produced when the nitrogen atoms of certain azo-derivatives are successively replaced by CH. J. B. T.

**Action of Orthamidophenol on Orthodiketones.** By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 343—344).—Orthamidophenol reacts with hydroxyquinones and with picrylic chloride in a manner analogous to the monalkyl-orthodiamines. With diacetyl, on the other hand, it behaves in a different manner.

Whilst orthamidodiphenylamine forms a substance of the formula  $\text{C}_{16}\text{H}_{14}\text{N}_2$ , containing no oxygen (*Abstr.*, 1892, 1108), orthamidophenol yields a substance of the formula  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ , which crystallises in plates with a satiny lustre and melts at 239—240°. It is insoluble in water, alkalis, and acids.

Phenanthraquinone also yields a colourless condensation product with orthamidophenol, although it has been found impossible to obtain one from benzile. A. H.

**Reduction of Aromatic Nitro-compounds.** By HANS LOESNER (*J. pr. Chem.*, 1894, [2], **50**, 563—567).—The author uses an alkali arsenite as a reducing agent; thus, to prepare azoxybenzene, nitrobenzene (25 grams), arsenious acid (30 grams), caustic soda (40 grams), and water (400 grams) are heated in a flask provided with a reflux condenser and a mechanical stirrer; after the contents have cooled, the oily layer of azoxybenzene is separated and, after slight acidification, distilled in steam; the yield is 60—70 per cent. of the theoretical. The author cannot confirm the statement that azoxybenzene yields benzidine when treated with sulphurous acid.

Metazoxybenzoic acid is prepared by heating sodium metanitrobenzoate with sodium arsenite in aqueous solution. *Parazoxybenzoic acid*, which has not been hitherto prepared, is made in the same way; it is a yellow amorphous powder, insoluble in most organic solvents, except pyridine.

It is to be noted that orthonitro-compounds resist the reducing action of alkali arsenites, so that it is possible to separate meta- and para- from ortho-nitro-compounds by submitting the mixture to the action of an alkali arsenite and subsequently removing the reduction products, leaving the orthonitro-compounds. A. G. B.

**Aromatic Diazo-compounds.** By HANS V. PECHMANN and LUDWIG FROBENIUS (*Ber.*, 1895, **28**, 170—176; compare *Abstr.*, 1894, i, 283).—

*Diazobenzeneparadiazotoluenetoluidide*,  $C_7H_7 \cdot N < \begin{smallmatrix} N:NPh \\ N:N \cdot C_7H_7 \end{smallmatrix}$ , seems to be formed when, in methyl alcoholic solution in the presence of sodium methoxide, diazobenzene acts on paradiazoamidotoluene, or paradiazotoluene on paradiazoamidobenzenetoluene, the latter being prepared either from diazobenzene and toluidine or from diazotoluene and aniline. It is a yellow, crystalline substance, and explodes at  $76^\circ$ . *Diazobenzeneparadiazotolueneanilide*,  $NPh < \begin{smallmatrix} N:NPh \\ N:N \cdot C_7H_7 \end{smallmatrix}$ , is obtained from paradiazotoluene and diazoamidobenzene; it crystallises in yellow needles, and explodes at  $72$ — $73^\circ$ .

Bisdiazobenzenamide and similar compounds (*Abstr.*, 1894, i, 329) might conceivably have unsymmetrical formulæ,  $NR \cdot N \cdot N \cdot N \cdot NHR$ , instead of  $NH(N \cdot NR)_2$ . But bisparadiazotolueneamide, when treated with sodium methoxide and methylic iodide, yields a methyl derivative which is identical with the bisdiazotoluenemethylamide,  $NMe(N \cdot NC_7H_7)_2$ , of Goldschmidt and Badl (*Abstr.*, 1889, 774); this speaks for the symmetrical structure of the original substance.

When paranitrodiazobenzene chloride is added to cooled concentrated ammonia, *paradinitrodiazoamidobenzene*,



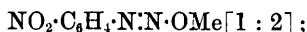
is formed; it crystallises in yellow needles and melts at  $228$ — $230^\circ$ . Probably the ammonium salt of the isodiazo-compound is first formed, and this yields the nitraniline, which then condenses with the diazo-chloride to form the diazoamido-compound.

Paranitrodiazobenzene methyl ether condenses much more readily with phenols than the sodium derivative of paranitroisodiazo benzene. It is not, therefore, like the latter substance, an isodiazo-compound, although Hantzsch thinks that it is. And in general the authors, in opposition to Hantzsch, regard the diazo- and isodiazo-compounds as structurally, and not merely geometrically, isomeric. C. F. B.

**Alkyllic Diazosalts.** By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 225—244).—These were prepared by allowing the alkyllic iodide in ethereal solution to remain, at  $0^\circ$  and in the dark, in contact with the normal silver diazo-salt,  $C_6H_5 \cdot N \cdot N \cdot OAg$ , or iso-diazo-salt,  $C_6H_5 \cdot NAg \cdot NO$ . Much iodo-compound (for example, iodobenzene) is also formed, especially when the normal diazo-salt is used; indeed the alkyllic salts can often only be prepared from the isodiazo-compounds, and yet their reactions show that they are all normal, and not iso-, diazo-compounds. Potash hydrolyses them to normal potassium diazo-salt (except when the latter is known to readily undergo a molecular transformation); boiling dilute sulphuric acid converts them into phenol, alcohol and nitrogen; and they condense, even at temperatures below the atmospheric, with aromatic amines to form diazoamido-compounds, and with  $\alpha$ -naphthylamine,  $\alpha$ -naphthol, and other aromatic bases and phenols, to form azo-colouring matters. There is not the least reason to suppose that a substance with the properties of

Hantzsch's "anti" alkylic diazo-salts is ever formed; and the isodiazocompounds are certainly nitrosamines, and structurally, not merely geometrically, isomeric with the normal diazo-compounds. The alkylic diazo-salts form in most cases colourless or yellowish oils; they are very unstable, and even explode if kept in tightly closed vessels. The following were prepared:—

*Diazobenzene methyl ether*,  $C_6H_5 \cdot N \cdot N \cdot OMe$ . *Parabromodiazobenzene methyl ether*,  $C_6H_4Br \cdot N \cdot N \cdot OMe$ . *Diazonaphthalene methyl ether*,  $C_{10}H_7 \cdot N \cdot N \cdot OMe$ . *Orthonitrodiazobenzene methyl ether*,



like the para-compound, undergoes molecular transformation when hydrolysed with potash, yielding the potassium iso-salt. *Orthonitrodiazamidobenzene*,  $NO_2 \cdot C_6H_4 \cdot N \cdot NHPh$  [1 : 2], crystallises in orange-yellow needles and melts at  $104.5-105^\circ$ . *Paranitrodiazobenzene ethyl ether*,  $NO_2 \cdot C_6H_4 \cdot N \cdot N \cdot OEt$  [1 : 4], crystallises in white, nacreous plates melting at  $24^\circ$ ; the *methyl ether* (compare Pechmann and Frobenius, Abstr., 1894, i, 283). *Orthomethylparanitrodiazobenzene methyl ether*,  $NO_2 \cdot C_6H_3Me \cdot N \cdot N \cdot OMe$  [N : Me :  $NO_2 = 1 : 2 : 4$ ], forms yellowish needles melting at  $94^\circ$ ; the *ethyl ether* is an oil. *Orthomethylparanitrodiazamidobenzene*,  $NO_2 \cdot C_6H_3Me \cdot N \cdot NHPh$ , crystallises in yellow needles, and melts at  $122^\circ$ . The author thinks that in normal diazo-salts (chlorides, &c.) the nitrogen atom joined to the negative group must be quinquivalent, as is indicated by the formula  $R \cdot N : N \cdot X$ , where the + and - ions are respectively ( $R \cdot N : N$ ) and X. Or the Blomstrand-Strecker-Erlenmeyer formula,  $N : NR \cdot X$ , might be given. To the "labile" (Hantzsch's "syn") potassium diazobenzenesulphonate might be assigned the formula  $NPh : N \cdot SO_3K$  [ions ( $NPh : N \cdot SO_3$ ) and K], or the V. Meyer-Jacobson formula,  $N : NPh \cdot SO_3K$ .  
C. F. B.

**d-Glucosebenzoylhydrazone.** By HEINRICH WOLFF (*Ber.*, 1895, 28, 160—163).—Aldoses react with acid hydrazides in accordance with the equation  $R \cdot CO \cdot NH \cdot NH_2 + O \cdot CH \cdot R' = R \cdot CO \cdot NH \cdot N \cdot CH \cdot R' + H_2O$ , when the two substances are heated together in alcoholic solution; the compounds formed crystallise in white needles, and are decomposed by boiling with water.

*d-Glucosephenylsulphonehydrazone*,  $Ph \cdot SO_2 \cdot NH \cdot N \cdot C_6H_{12}O_5$ , melts with decomposition at  $154-155^\circ$ ; boiling with water converts it into dextrose, biphenylsulphonehydrazone,  $N_2H_2(SO_2Ph)_2$ , (and hydrazine?), a violent evolution of gas taking place.

*d-Glucosebenzoylhydrazone*,  $CPhO \cdot NH \cdot N \cdot C_6H_{12}O_5$ , melts and decomposes at  $171-172^\circ$ ; boiling with water converts it into *d*-glucose and benzoylhydrazine. The latter can be precipitated as benzylidenebenzoylhydrazine by the addition of benzaldehyde, and the *d*-glucose can then be recovered from the solution. These reactions afford a means of isolating *d*-glucose from invert-sugar, for *l*-fructose, being a ketose and not an aldose, does not react with benzoylhydrazine.

C. F. B.

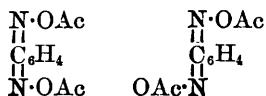
**Reduction of Aromatic Nitro-compounds.** By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 245—251; compare *Abstr.*, 1894, i, 373).—A preliminary notice, published prematurely owing to invasion of the author's territory by Lumière and Seyewetz (*Bull. Soc. Chim.*, 1894, [3], **11**, 1038). *Paratolylhydroxylamine*,  $C_6H_4Me \cdot NH \cdot OH$  [1 : 4], forms nacreous plates, melting at  $93.5-94^\circ$ ; it oxidises in air to *para*-azoxytoluene, and is converted by nitrous acid into a *nitrosamine*, which crystallises in white needles melting at  $59-59.5^\circ$ , and further into *paradiazotoluene* nitrate; hot dilute sulphuric acid converts it into *paratoluquinol* [ $Me : (OH)_2 = 3 : 1 : 4$ ]; and oxidising agents into *paranitrosotoluene*,  $C_6H_4Me \cdot NO$ , which crystallises in white needles, melts at  $48.5^\circ$  to a green liquid, and yields green solutions.

*Metatolylhydroxylamine* crystallises in white, silky plates, and melts at  $68^\circ$ . The *nitrosamine* crystallises in white needles, which melt at  $54-54.5^\circ$ ; *metanitrosotoluene* forms white needles which melt at  $53-53.5^\circ$  to a green liquid, and yield green solutions.

*Orthotolylhydroxylamine* is an oil, and yields a *nitrosamine*. *Ortho*-*nitrosotoluene* crystallises in white needles, melts at  $72-72.5^\circ$  to a green liquid, and yields green solutions.

Nitro-derivatives of halogenbenzenes, of benzylic chloride, of benzaldehyde, and of benzoic acid appear to yield hydroxylamines when boiled with zinc dust and water. Nitranilines are reduced to diamines, and nitrophenols to amidophenols. C. F. B.

**Stereoisomeric Derivatives of Quinonedioximes.** By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 340—343).—Diacetylquinonedioxime exists in two isomeric forms. The more stable of these is formed when quinonedioxime is boiled with sodium acetate and acetic anhydride for some minutes. It crystallises in compact, leaf-like plates, is only sparingly soluble in benzene, and melts at  $190^\circ$ . The less stable form is obtained when the mixture of quinonedioxime, sodium acetate, and acetic anhydride is heated just to boiling, and then immediately cooled. It is readily soluble in benzene, from which it crystallises in long, lustrous needles containing benzene, but the latter is rapidly lost on exposure to the air. It melts at  $147^\circ$ , when rapidly heated, but the melting point quickly rises, owing to partial conversion into the isomeride. When boiled with benzene for some time, it is also converted into the isomeride. Both the forms have the normal molecular weight as determined by the cryoscopic method, and both yield the same quinonedioxime when hydrolysed. It is probable that the substance of lower melting point is the syn-derivative, the higher being the anti-form.



Thymoquinone also appears to yield two isomeric acetates. Quinonedioxime itself is known to crystallise in two different forms, but it is at least doubtful whether these are stereoisomeric modifications.

A. H.

**Imidazolones and their Decomposition Products.** By HANS RUPE (*Ber.*, 1895, **28**, 251—260; compare *Abstr.*, 1894, i, 241).—Formylbenzoylcarbamide,  $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHO}$ , is formed by the action of nitric acid of sp. gr. 1.405 on phenylimidazolone in acetic acid solution. It crystallises in long, flat needles melting at  $161^\circ$ . When boiled with dilute alcoholic hydrogen chloride, or treated with cold aqueous soda, it is converted into formic acid and benzoylcarbamide, which melts, when pure, at  $215^\circ$ , and not at  $208^\circ$ , as hitherto supposed (*Zeit. f. Chem.*, 1868, 305).

If only 1 mol. of nitric acid be employed, nitrophenylimidazolone is formed. This crystallises in lustrous, yellow plates, which decompose at  $203\text{--}207^\circ$ , according to the rapidity with which they are heated. This substance has acid properties, and is not altered by boiling with water or dilute alkalis, although with acids a deep-seated decomposition takes place after some time.

Bromine reacts with phenylimidazolone to produce the *ureide* of *parabromobenzoylformic acid*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , which forms small, lustrous prisms melting at  $186.5^\circ$ . It is very stable towards acids, and dissolves without alteration in dilute alkalis, but is decomposed when boiled with them, carbamide being produced, along with benzoylformic acid. The *hydrazone* of the ureide crystallises in slender, yellow needles, and melts at  $151^\circ$ . On reduction with sodium amalgam at  $40^\circ$ , the ureide is quantitatively converted into carbamide and mandelic acid. *Parabromobenzoylformic acid* forms small plates, which have a satiny lustre, and melt at  $108^\circ$ . The *sodium* salt is only sparingly soluble in water, and is precipitated from a concentrated solution of the acid by aqueous soda. The acid, like benzoylformic acid itself, gives a reddish-violet coloration with sulphuric acid and benzene containing thiophen. The *hydrazone* of the acid forms yellow needles melting at  $180.5^\circ$ . The acid is reduced by sodium amalgam to mandelic acid, and is oxidised by silver oxide to parabromobenzoic acid, its constitution, and that of the ureide, being thus proved.

*Methylic parabromobenzoate* crystallises in long, white needles, has an extremely pleasant, fruity odour, and melts at  $81^\circ$ . A. H.

**Oil of Mignonette Root.** By JULIUS BERTRAM and HEINRICH WALBAUM (*J. pr. Chem.*, 1894, [2], **50**, 555—561).—The root of *Reseda odorata*, L., yields an oil, on distillation, which smells of radishes, has a light brown colour, a sp. gr. of 1.067 at  $15^\circ$ , and a rotation of  $+1^\circ 30'$  in a 100-mm. tube. This oil is phenylethylthiocarbimide, for, when heated with strong hydrochloric acid, it yields phenylethylamine hydrochloride, carbon oxysulphide and hydrogen sulphide being evolved; phenylethylthiocarbamide is produced when it is heated with alcoholic ammonia. The authors find that diphenylethylloxamide melts at  $186^\circ$ , and phenylethylthiocarbamide at  $137^\circ$ , whilst Neubert (*Abstr.*, 1886, 873) gives  $180^\circ$  and  $123^\circ$  respectively for these constants. They have synthesised phenylethylthiocarbimide, and find that its reactions are in accord with those of mignonette-root oil. A. G. B.



**Isophenolphthaleïn and Allofluoresceïn.** By BRONISLAW PAWL-EWSKI (*Ber.*, 1895, **28**, 108—109).—In this preliminary notice, the author describes compounds obtained by the action of phthalic chloride on phenols, and isomeric with the phenolphthaleïns.

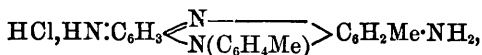
*Isophenolphthaleïn* crystallises in slender, white needles melting at 69—70°, and is not coloured by alkalis. Its constitution is probably represented by the formula  $\text{CO} \langle \overset{\text{O}}{\text{C}_6\text{H}_4} \rangle \text{C}(\text{OPh})_2$ . Catechol and quinol react with 1 mol. of the chloride to form substances of a similar constitution. Resorcinol, on the other hand, yields two compounds,  $\text{CO} \langle \overset{\text{O}}{\text{C}_6\text{H}_4} \rangle \text{C} \langle \overset{\text{O}}{\text{O}} \rangle \text{C}_6\text{H}_4$  and  $\text{CO} \langle \overset{\text{O}}{\text{C}_6\text{H}_4} \rangle \text{C}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$ . These both give green, fluorescent solutions with potash, but differ markedly from fluoresceïn itself. A. H.

**Constitution of the Safranines.** By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 270—276).—The action of nitrosodimethylaniline hydrochloride on metahydroxydiphenylamine yields a black colouring matter which probably belongs to the oxazine group. In the presence of a mineral acid, on the other hand, a carmine-red colouring matter, *dimethylsafraninone*,  $\text{O} \cdot \text{C}_6\text{H}_3 \langle \overset{\text{N}}{\text{NPh}} \rangle \text{C}_6\text{H}_3 \cdot \text{NMe}_2 \cdot \text{HCl}$ , is formed; this is a brownish-red, crystalline powder, which yields a red solution with water, and dissolves in alcohol forming an orange-red solution with a yellow fluorescence. Aqueous soda precipitates the base, which is of no industrial importance. The formation of the substance takes place in two stages, a blue indophenol being formed as an intermediate product.

*Safraninone*,  $\text{O} \cdot \text{C}_6\text{H}_3 \langle \overset{\text{N}}{\text{NPh}} \rangle \text{C}_6\text{H}_3 \cdot \text{NH}_2 \cdot \text{HCl}$ , may be obtained in a similar manner, but is best prepared by the oxidation of a mixture of paraphenylenediamine and metahydroxydiphenylamine in molecular proportion; it is also formed in very small quantity when safranin is heated with ammonia at 180°. The crystals have a green lustre, but in other respects resemble those of the dimethyl-derivative. It contains an amido-group, and forms a blue diazo-compound, which reacts with  $\beta$ -naphthol to form a blue colouring matter. When the amido-group is eliminated, *safranone*,  $\text{O} \cdot \text{C}_6\text{H}_3 \langle \overset{\text{N}}{\text{NPh}} \rangle \text{C}_6\text{H}_4$ , is produced; this is also formed when “safranid” (azosafranin) is heated with 75 per cent. sulphuric acid. It crystallises in small, brown needles, and yields a magenta-coloured solution with hot water. All the three compounds just described exhibit dichroïsm when dissolved in concentrated sulphuric acid.

*Safranin*,  $\text{O} \cdot \text{C}_6\text{H}_3 \langle \overset{\text{N}}{\text{NPh}} \rangle \text{C}_6\text{H}_3 \cdot \text{OH}$ , is formed when metahydroxydiphenylamine is heated with paranitrosophenol and aqueous soda, and may also be obtained by oxidising a mixture of paramidophenol and metahydroxydiphenylamine in presence of mineral acids. The formation of safranin by these methods supplies the proof that safranin contains the amido-group in the meta-position.

A safranine synthesis can be carried out, in complete agreement with this conclusion, by heating metamidoditolylamine, obtained from paradiitolylamine, with quinone dichlorimide in acetic acid solution. The new safranine has the formula



and is isomeric with the safranine T of commerce. It is obtained as the hydrochloride, and forms a beetle-green powder, which yields fluorescent solutions. The colour produced on cotton mordanted with tannin cannot be distinguished from that obtained with safranine T.

A. H.

**The Fluorindines.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1895, 28, 293—301; compare *Abstr.*, 1890, 1444).—The red oxidation product of orthamidophenol, described by Fischer and Jonas (this vol., i, 25) as having the formula  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ , is identical with the compound obtained by Zincke and Hebebrand (*Abstr.*, 1885, 258) by the oxidation of the same substance with quinone, to which, however, they assigned the formula  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4$ . The determination of the molecular weight by the cryoscopic method, using phenol as a solvent, shows that the molecular formula is  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ , so that the substance is probably amidobenzeneazoxindone. It contains a primary amido-group, and reacts with aldehydes like a primary base. The compound thus formed with salicylaldehyde crystallises in needles, which have a golden lustre, and melt above  $300^\circ$ . When the red compound is fused with orthamidophenol hydrochloride, it yields triphenodioxazine, as previously described.

*Triphenazinoxazine*,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{NH} \\ \text{N} \end{array} \right\rangle \text{C}_6\text{H}_2 \left\langle \begin{array}{c} \text{N} \\ \text{O} \end{array} \right\rangle \text{C}_6\text{H}_4$ , is readily formed when asymmetric dioxyphenazine is treated in the same manner, and when the red compound, described above, is fused with orthophenylenediamine. It forms indistinctly crystalline aggregates, and yields fluorescent solutions.

Diphenylhomofluorindine (fluorindine) may be synthetically obtained by fusing the oxidation product of orthamidodiphenylamine (diphenyldiamidophenazine) with orthophenylenediamine hydrochloride. A good yield of the fluorindine is thus obtained.

Fluorindine can also be obtained synthetically by the oxidation of phenylinduline, dissolved in nitrobenzene, with mercuric oxide. A 10 per cent. yield is obtained, and the nitrobenzene seems to influence the reaction, as when other solvents are used a different fluorindine is obtained.

Fluorindine is, however, best prepared by oxidising, with mercuric oxide, azophenue dissolved in nitrobenzene.

The authors also maintain the formulæ which they have ascribed to triphenodioxazine, homofluorindine, and the fluorindines, against the criticism of Nietzki (*Chemie der organ. Farbstoffe*, II, Aufl., p. 230).

A. H.

**Iodonium Bases from Parachloriodobenzene.** By L. W. WILKINSON (*Ber.*, 1895, **28**, 99—101).—*Iododichlorodiphenyliodonium hydroxide*,  $C_6H_5ICl \cdot I(OH) \cdot C_6H_4Cl$ , prepared in a similar manner to the diphenyl compound (*Abstr.*, 1894, i, 461), is only known in aqueous solution. The *iodide* is colourless and crystalline, becomes yellow on exposure to air, and melts and decomposes at  $133^\circ$ . The *chloride* forms colourless plates, and the *bromide* granular crystals, melting at  $195^\circ$  and  $190^\circ$  respectively. The *nitrate* crystallises in colourless needles, melting and decomposing at  $188^\circ$ . The *periodide* forms brown, lustrous needles melting at  $152^\circ$ . The *sulphide* is yellow and unstable; the *platinochloride* is deposited in reddish-yellow crystals, and melts at  $160^\circ$ .

*Dichlorodiphenyliodonium hydroxide*,  $OH \cdot I(C_6H_4Cl)_2$ , obtained together with the preceding base, only exists in aqueous solution. The *iodide* forms colourless, flocculent crystals melting at  $163^\circ$ . The *chloride* crystallises in colourless plates, the *bromide* and *nitrate* in needles, they melt at  $202^\circ$ ,  $190^\circ$ , and  $200^\circ$  respectively. The *dichromate* is orange-yellow, unstable, and melts and decomposes at  $149^\circ$ . The *mercuriochloride* is deposited in colourless, flocculent crystals, the *platinochloride* in reddish needles; they melt at  $169^\circ$  and  $184^\circ$  respectively.

J. B. T.

**Iodonium Bases from Pariodotoluene.** By JOHN McCRAE (*Ber.*, 1895, **28**, 97—99).—The following compounds were prepared in a similar manner to the phenyl derivatives described by Hartmann and v. Meyer (*Abstr.*, 1894, i, 461). *Ditolyliodonium hydroxide*,  $OH \cdot I(C_6H_4Me)_2$ , is only known in aqueous solution, and is formed in small quantity in the preparation of iodo- and iodoso-toluene. The *iodide* is colourless, becomes yellow on exposure to light, and melts at  $146^\circ$ . The *chloride* and *bromide* crystallise in needles and both melt at  $178^\circ$ . The *dichromate* is deposited in reddish-yellow plates, and explodes when heated. The *periodide* crystallises in highly lustrous, dark red needles, and melts at  $156^\circ$ . The *nitrate*, *mercuriochloride*, and *bromo-mercuriochloride* crystallise in needles, and melt at  $139^\circ$ ,  $179^\circ$ , and  $189^\circ$  respectively. The *aurochloride* and *platinochloride* are deposited in plates; the former melts at  $126^\circ$ , the latter at  $176^\circ$ , with decomposition. By the action of sodium or ammonium sulphide on ditolylidonium hydroxide, iodotoluene, and paraditolyl sulphide are formed in the proportion of two molecules to one.

The base,  $C_6H_5IMe \cdot I(OH) \cdot C_6H_4Me$ , is only known in aqueous solution. The *iodide* melts and decomposes at no definite temperature. The *chloride* and *bromide* are amorphous, and melt at  $165.5^\circ$  and  $163^\circ$  respectively. The *dichromate* is unstable, and melts at  $154^\circ$ ; the *mercuriochloride* crystallises in small plates, and melts and decomposes at  $149^\circ$ .

J. B. T.

**Derivatives of Paradimethylamidobenzaldehyde.** By FRITZ BENDER (*Ber.*, 1895, **28**, 109—111).—Möhlau has described two colouring matters obtained by the action of dimethylaniline on nitrosodimethylaniline in hydrochloric acid solution in the presence of formaldehyde. The first of these, rubifuscine, to which he ascribed the

constitution of hexamethyltriamidophenylacridine, is decomposed, when the hydrochloride is boiled with water, into paradimethylamidobenzaldehyde and phenylenediamine. The second compound, named by Möhlau octomethyltetramidophenylacridine, is decomposed under similar conditions into dimethylamidobenzaldehyde and paramidodimethylaniline. The two colouring matters are, moreover, formed when the aqueous solutions of the hydrochlorides of their decomposition products are mixed. A. H.

**Paraïsobutylsalicylaldehyde and its Derivatives.** By F. B. DAINS and I. R. ROTHROCK (*Amer. Chem. J.*, 1894, **16**, 634—645; compare Bradley, *Abstr.*, 1892, 1458).—*Paraïsobutylsalicylaldehyde*,  $C_4H_9 \cdot C_6H_3(OH) \cdot COH$  [ $OH : COH : C_4H_9 = 1 : 2 : 4$ ], is obtained on heating a mixture of isobutylphenol (45 grams), sodium hydroxide (45 grams), chloroform (55 grams), and water (500 c.c.) in a water bath for two hours. The aldehyde is readily separated from the unchanged isobutylphenol by treating the product with phenylhydrazine, which gives with the former a well-characterised solid hydrazone. This is readily reconverted into the aldehyde on treatment with sulphuric acid and subsequent steam distillation. The pure aldehyde is a yellow, highly refractive oil, with an aromatic odour resembling that of salicylaldehyde. It boils, decomposing slightly, at  $251-252^\circ$  under a pressure of 729 mm., and does not solidify at  $-18^\circ$ ; sp. gr. = 1.039 at  $20^\circ$ . It dissolves in all the common organic solvents, and forms a violet-coloured solution with ferric chloride. From a neutral solution of the sodium derivative, copper sulphate throws down a yellowish-green precipitate, and silver nitrate, lead acetate, calcium chloride, and barium chloride throw down white precipitates. The *phenylhydrazone*,  $C_4H_9 \cdot C_6H_3(OH)CH:N \cdot NPh$ , crystallises from light petroleum in thin, golden, monoclinic plates, melts at  $178^\circ$ , and yields a *diacetyl derivative*,  $C_4H_9 \cdot C_6H_3(OAc)CH:N \cdot NAcPh$ , which crystallises in small, white needles, and melts at  $128^\circ$ . The *aniline derivative*,



crystallises from alcohol in yellow, monoclinic plates, and melts at  $87^\circ$ . The *aldoxime*,  $C_4H_9 \cdot C_6H_3(OH)CH:NOH$ , crystallises from light petroleum in long, monoclinic needles, melts at  $112^\circ$ , yields a *dibenzoyl derivative* which melts at  $160^\circ$ ; and, on treatment with acetic anhydride, forms the *acetyl derivative* of *paraïsobutylsalicylonitrile*,  $C_4H_9 \cdot C_6H_3(OAc) \cdot CN$ , a pale yellow oil, which on hydrolysis with potash forms *paraïsobutylsalicylonitrile*,  $C_4H_9 \cdot C_6H_3(OH) \cdot CN$ ; this crystallises in slender, white, monoclinic needles.

The *methyl derivative* of *paraïsobutylsalicylaldehyde* boils at  $274-276^\circ$ , at a pressure of 735 mm., the *benzyl derivative* crystallises in long, slender, monoclinic prisms, which melt at  $70-71^\circ$ . *Ethyl paraïsobutylsalicylaldehydecaboxylate*,  $COH \cdot C_6H_3(C_4H_9) \cdot COOEt$ , melts at  $63^\circ$ . *Paraïsobutylidisalicylaldehyde* crystallises in monoclinic needles, and melts at  $158^\circ$ .

*Paraïsobutylorthobromosalicylaldehyde* [ $OH : COH : C_4H_9 : Br = 1 : 2 : 4 : 6$ ], obtained by the action of bromine on the dried sodium

derivative of paraïsobutylsalicylaldehyde, suspended in carbon bisulphide, crystallises in pale yellow, monoclinic plates, and melts at  $86-87^{\circ}$ ; the corresponding *aldoxime* crystallises in white, tabular, monoclinic plates, melts at  $163^{\circ}$ , and forms a *dibenzyl* derivative, which crystallises from hot alcohol in needles and melts at  $189^{\circ}$ ; the corresponding *phenylhydrazone* forms long, monoclinic crystals, and melts at  $152^{\circ}$ .  
G. T. M.

**Constitution of the Bromocinnamic acids.** By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 134—137).—Glaser's  $\alpha$ -bromocinnamic acid is converted, although with some difficulty, into ordinary cinnamic acid when it is boiled in alcoholic solution with zinc filings. This acid therefore has the stereochemical formula  $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{H} \\ | \\ \text{Br}\cdot\text{C}\cdot\text{COOH} \end{array}$ , which agrees well with its reactions and transformations. A. H.

**Intramolecular Change in  $\beta\gamma$ -Phenylcrotonic acid.** By RUDOLPH FITTIG and ALFONS LUIB (*Annalen*, 1894, **283**, 297—308).—Amongst the unsaturated  $\beta\gamma$ -acids which have been investigated, phenylcrotonic acid is distinguished by its stability towards aqueous soda, scarcely more than 10 per cent. being attacked by this reagent after many hours.  $\alpha\beta$ -Phenylcrotonic acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}:\text{CH}:\text{COOH}$ , is one of the products, the yield of this substance amounting to about 1 per cent. It crystallises from benzene in nacreous plates, and melts at  $65^{\circ}$ . The calcium salt contains  $3\text{H}_2\text{O}$ , and the barium salt  $1\text{H}_2\text{O}$ . Phenyl- $\beta$ -bromobutyric acid crystallises in short, transparent prisms, and melts at  $54^{\circ}$ . It dissolves in boiling water, giving rise to phenylpropylene and phenyl- $\beta$ -hydroxybutyric acid, which is also formed by the action of boiling aqueous soda on  $\beta\gamma$ -phenylcrotonic acid; this crystallises from ether in colourless plates and melts at  $98^{\circ}$ . When distilled, it gives rise to a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -isocrotonic acids. The calcium salt is anhydrous, and the barium salt contains  $1\text{H}_2\text{O}$ ; the silver salt crystallises from hot water in thin plates. A mixture of  $\alpha\beta$ - and  $\beta\gamma$ -phenylcrotonic acids, in which the latter preponderates, is formed when phenyl- $\beta$ -hydroxybutyric acid is treated with hot aqueous soda for 12 hours; 90 per cent. of unchanged acid is recoverable. M. O. F.

**Intramolecular Change in Phenyl- $\beta\gamma$ -pentenic (Hydrocinnamenylacrylic) acid.** By RUDOLPH FITTIG and THEODOR HOFFMANN (*Annalen*, 1894, **283**, 308—318; compare R. Fittig and J. Stern, *Abstr.*, 1892, 988).—Phenyl- $\alpha\beta$ -pentenic acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}:\text{COOH}$ , is readily formed when hot aqueous soda acts on the  $\beta\gamma$ -acid. It melts at  $104^{\circ}$  and forms rhombic crystals;  $a:b:c = 0.5863:1:0.2675$ . The calcium salt crystallises in prismatic needles which retain  $3\text{H}_2\text{O}$ ; the barium salt contains  $4\text{H}_2\text{O}$ . The silver salt crystallises from hot water. The calcium salt of the  $\beta\gamma$ -acid contains  $1\text{H}_2\text{O}$ , and the barium salt is anhydrous.

Phenyl- $\alpha\beta$ -dibromovaleric acid crystallises in slender needles, which melt at  $139^{\circ}$  (following abstract); sodium amalgam reduces it to

phenylvaleric acid. *Phenyl-β-bromovaleric acid* melts at 57—58°. Boiling water converts it into *phenyl-β-hydroxyvaleric acid*, which is also formed by the action of hot aqueous soda on phenyl-β-γ-pentenic acid; it separates from water and from ether in prismatic crystals, which melt at 131°. The *calcium* salt is anhydrous, and the *barium* salt retains 1H<sub>2</sub>O. Phenyl-β-hydroxyvaleric acid is attacked slowly by hot aqueous soda, yielding 10 per cent. of phenyl-αβ-pentenic acid; which is also formed when the hydroxy-acid is distilled. M. O. F.

**Brominated Acids from Phenyl-αβ-pentenic and Phenyl-β-γ-pentenic acids.** By RUDOLPH FITTIG and HEINRICH PERRIN (*Annalen*, 1894, 283, 318—337; compare the preceding abstract, and R. Fittig and J. Stern, *Abstr.*, 1892, 988).—When the solution of phenyl-β-bromovaleric acid in warm petroleum is allowed to evaporate spontaneously, two forms of crystals are deposited; one modification melts at 55—56°, whilst the other sinters at 57°, and melts completely at about 80°.

Treatment with boiling water for several hours converts phenyl-β-bromovaleric acid into a mixture of phenylbutylene, phenyl-β-hydroxyvaleric acid, phenyl-αβ-pentenic acid, and a very small quantity of phenylvalerolactone.

The action of bromine on hydrocinnamylacrylic acid gives rise to phenyl-β-γ-dibromovaleric acid, which melts at 111—112°, and crystallises in plates belonging to the asymmetric system;  $a : b : c = 1.538 : 1 : 2.41577$ . This acid is also formed when cinnamylacrylic acid is acted on by hydrogen bromide, and when thus obtained, it melts at 113.5—114.5°; this form is less soluble than the modification of lower melting point, from which it differs also crystallographically. The crystals belong to the monosymmetric system;  $a : b : c = 2.0548 : 1 : 1.2052$ .  $\beta = 69^\circ 30'$ . When boiled with aqueous sodium carbonate, it yields an unsaturated hydrocarbon and an acid which crystallises from boiling water in needles, and melts at 138°; *phenyl-pentenolactone*, C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>, is formed at the same time. This crystallises in plates which melt at 60°, and differs completely from phenyl-angelicalactone obtained from the isomeric dibromo-acid under similar conditions (*loc. cit.*). Hot aqueous alkalis convert it into salts of *phenylhydroxypentenic acid*; the *barium* and *calcium* salts are anhydrous, and the *silver* salt is decomposed by light. Phenyl-pentenolactone is unsaturated, and when treated with bromine yields *phenyldibromovalerolactone*, C<sub>11</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>2</sub>, which crystallises in silvery plates and melts at 99—100°.

*Phenyltetrabromovaleric acid* is obtained by the action of bromine on cinnamylacrylic acid; it forms a crystalline powder which melts at 243°, with copious evolution of gas.

*Phenyldibromopentenic acid*, CHPh·CH·CHBr·CHBr·COOH, is obtained by adding to the solution of cinnamylacrylic acid in ether and carbon bisulphide the calculated amount of bromine in the latter solvent; it forms colourless, transparent crystals, which lose hydrogen bromide when recrystallised. M. O. F.

**Oxidation Products of Phenyl- $\beta$ - $\gamma$ -pentenic and Phenyl- $\alpha$ - $\beta$ -pentenic acids.** By RUDOLPH FITTIG and ERNST MAYER (*Annalen*, 1894, **283**, 337—341; compare Abstr., 1892, 986).—Phenyl- $\beta$ - $\gamma$ -dihydroxyvaleric acid (*loc. cit.*) crystallises in long needles which melt at  $110^{\circ}$ , readily undergoing conversion into phenylvalerolactone.

Phenyl- $\alpha$ - $\beta$ -dihydroxyvaleric acid is obtained by oxidising phenyl- $\alpha$ - $\beta$ -pentenic acid with potassium permanganate; it crystallises from water in needles, and melts at  $156.5^{\circ}$  without giving rise to the lactone. The barium salt is anhydrous, and the calcium salt forms colourless, silky plates which contain  $1\text{H}_2\text{O}$ ; the silver salt is a crystalline powder.

M. O. F.

**$\alpha$ - and  $\beta$ -Isatropic acids.** By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 137—143).—When  $\alpha$ -isatropic acid, dissolved in alcohol, is treated with hydrogen chloride, without cooling, ethylic hydrogen isatropate,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{COOEt}$ , separates; it crystallises in small plates melting at  $186^{\circ}$ . When boiled with aqueous 33 per cent. potash, it is converted into a mixture of 1 part of  $\alpha$ -isatropic acid and 2 parts of  $\beta$ -isatropic acid. When  $\beta$ -isatropic acid is treated with hydrogen chloride in a similar manner, a substance is obtained which, on decomposition with potash, yields  $\beta$ -isatropic acid. After repeated crystallisation from acetic acid, however, this becomes identical with the ethylic hydrogen isatropate obtained directly from  $\alpha$ -isatropic acid, and behaves in the same manner towards aqueous potash. It is therefore probable that ethylic hydrogen  $\beta$ -isatropate is first formed and is then converted by repeated crystallisation into the corresponding  $\alpha$ -compound.

If  $\alpha$ -isatropic acid is heated at  $70^{\circ}$  with alcoholic hydrogen chloride, a normal ethylic salt,  $\text{C}_6\text{H}_4(\text{COOEt})_2$ , is formed; this substance melts at  $78$ — $79^{\circ}$ , whereas, according to Fittig (*Annalen*, **206**, 34), normal ethylic  $\alpha$ -isatropate melts at  $180$ — $181^{\circ}$ , and is formed by simply passing hydrogen chloride into an alcoholic solution of the acid. The normal ethylic salt obtained by the author yields, on hydrolysis with alcoholic potash, a mixture of acids containing about 20—30 per cent. of the  $\alpha$ -acid and 80—70 per cent. of the  $\beta$ -acid. It seems probable that the relations between these two acids are to be explained by stereochemical considerations, and, indeed, an examination of the formulæ put forward as probable by Fittig shows that cis-trans-isomerism is possible. The author's researches in this direction are not yet completed.

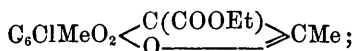
A. H.

**Condensation of Toluquinone with Ethylic Acetoacetate.** By CARL GRAEBE and SIEGMUND LEVY (*Annalen*, 1894, **283**, 245—268).—

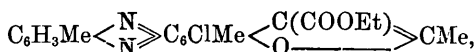
Hydroxydimethylisocoumarilic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me} < \text{O} \begin{array}{c} \text{C}(\text{COOH}) \\ \text{O} \end{array} \text{CMe}$ , crystallises in needles which decompose at  $280^{\circ}$ . It is obtained from the ethylic salt, which is produced when a mixture of toluquinone and ethylic acetoacetate is heated with acetone and zinc chloride; it crystallises in colourless pyramids which melt at  $173^{\circ}$ , and it dissolves in concentrated sulphuric acid, with development of an intense blue coloration which gradually becomes brown. The ethylic salt gives rise

to an *acetyl* derivative which crystallises in large, colourless needles, and melts at  $96^{\circ}$ ; the *benzoyl* derivative melts at  $94-95^{\circ}$ . The *bromo*-derivative melts at  $208^{\circ}$ , and yields an *acetyl* derivative which melts at  $137-138^{\circ}$ . The  *dibromo*-derivative melts at  $123-124^{\circ}$ , and the *tribromo*-derivative  $145^{\circ}$ ; these derivatives also have been acetylated. The *dichloro*-derivative melts at  $134-135^{\circ}$ , and yields an *acetyl* derivative which melts at  $138-139^{\circ}$ ; it is converted by the action of 10 per cent. aqueous soda into *hydroxydimethyldichlorocoumarilic acid*, which decomposes at  $260-270^{\circ}$  and yields a *barium* salt containing  $2\text{H}_2\text{O}$ . The *trichloro*-derivative,  $\text{O}:\text{C}_6\text{Cl}_3\text{Me} < \underset{\text{O}}{\text{C}}(\text{COOEt}) > \text{CMe}$ , melts at  $103^{\circ}$ .

The *dichloro*- and *trichloro*-derivatives, when oxidised with dilute nitric acid, yield the *orthoquinone* derivative of the ethylic salt of dimethylchlorisocoumarilic acid, which has the constitution

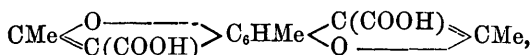


it crystallises in deep red plates which melt at  $118-119^{\circ}$ , and dissolves in concentrated sulphuric acid with development of a violet coloration gradually changing to dark blue. On reducing this compound, dihydroxydimethylchlorisocoumarilic acid is obtained in the form of the *ethylic* salt; this melts at  $170-171^{\circ}$ , and yields a *diacetyl* and a *dibenzoyl* derivative which melt at  $136^{\circ}$  and  $174-175^{\circ}$  respectively. The *quinoxaline* derivative,



is obtained by the action of orthotoluylenediamine on the *ethylic* salt. It crystallises in reddish-violet needles melting at  $162^{\circ}$ .

The *ethylic* salt of trimethylbenzodifurfuranedicarboxylic acid,



is formed, in addition to the *ethylic* salt of hydroxydimethylisocoumarilic acid, when a mixture of toluquinone and *ethylic* acetoacetate is heated with zinc chloride. It melts at  $133^{\circ}$ , and gives rise to a *bromo*-derivative. The *acid* itself is obtained in needles which melt at  $220^{\circ}$ ; the *potassium* salt is anhydrous, and the *sodium* salt contains  $4\text{H}_2\text{O}$ .  
M. O. F.

**Iodoisophthalic and Iodosoisophthalic acids.** By ALBERT GRAHL (*Ber.*, 1895, 28, 84-90).—*Meta-iodoisophthalic acid*,  $[(\text{COOH})_2 : \text{I} = 1 : 3 : 5]$ , is prepared from the corresponding nitroisophthalic acid, and crystallises from acetic acid in lustrous, microscopic needles melting at  $288-289^{\circ}$ . The *silver* salt is amorphous. When *potassium permanganate* acts on the acid, in presence of sulphuric acid, no *iodoso*-derivative is formed, but the bulk of the acid is completely oxidised, and the remainder recovered unchanged. The *nitro*-deriva-



tive crystallises in slender, yellow needles. The *iododichloride*, formed by the action of chlorine on the acid in chloroform solution, is yellow, amorphous, and unstable; on treatment with soda, the original acid is regenerated.

*Pariodometatoluic acid*,  $[\text{COOH} : \text{Me} : \text{I} = 1 : 3 : 4]$ , is prepared by the oxidation of 1 : 3 : 4-iodo-xylene with nitric acid; it melts at  $214-215^\circ$ , and is identical with the acid mistaken for "iodoisophthalic acid" by Hammerich (Abstr., 1890, 1106). The *silver salt* is amorphous; the *iododichloride* is amorphous and unstable.

*Orthiodoisophthalic acid*,  $[(\text{COOH})_2 : \text{I} = 1 : 3 : 4]$ , is obtained when the preceding acid is oxidised with potassium permanganate; it is purified by means of the dimethylic salt, and melts at  $285-286^\circ$ . The *silver salt* is amorphous.

*Orthiodosoisophthalic acid*,  $\text{C}_6\text{H}_3(\text{COOH})_2\cdot\text{IO}$ , is formed by the action of concentrated nitric acid on the iodo-acid, and crystallises in colourless, lustrous needles melting and decomposing at  $269^\circ$ ; it readily reacts with potassium iodide at the ordinary temperature, and in general properties resembles the corresponding benzoic and terephthalic acids. The *hydrogen sodium salt* crystallises with  $1\text{H}_2\text{O}$  in yellow plates; the *hydrogen silver salt* is yellow and amorphous, and explodes when heated.

The acid termed by Klingel "orthiodoisophthalic acid" (Abstr., 1886, 61) is evidently some other compound, as it melts at  $203-204^\circ$ .

J. B. T.

**Action of Bromine on Alkylidenemalononic acids and their Ethereal Salts.** By CARL T. LIEBERMANN (*Ber.*, 1895, 28, 143—145). —The author has confirmed the statement made by Claisen and Crismer (Abstr., 1884, 444) that benzylidenemalononic acid does not form an additive compound with bromine, whilst its ethylic salt does so slowly. This appears to be a general property of unsaturated compounds containing a doubly linked carbon atom combined with two carboxyl or similar electronegative groups. The feeble additive powers of such unsaturated acids as fumaric acid, mesaconic acid, &c., are probably to be ascribed to a similar cause, the electronegative groups being in these cases each combined with one of the doubly linked carbon atoms.

A. H.

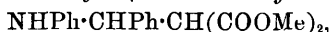
**Addition of Aniline and Phenylhydrazine to Methylic Benzylidenemalonate.** By R. BLANK (*Ber.*, 1895, 28, 145—148). —It is already known that ethylic salts of the type  $\text{R}\cdot\text{CH}\cdot\text{C}(\text{COOR})_2$ , not only form bimolecular polymerides, but also additive compounds with 1 mol. of water, ethylic alcohol, sodium ethoxide, sodium methoxide, or ethylic malonate. It is now shown that additive compounds are also formed with aniline and phenylhydrazine.

Aniline unites with methylic hydrogen benzylidenemalonate,  $\text{CHPh}\cdot\text{C}(\text{COOMe})\cdot\text{COOH}$ , to form the *aniline salt of methylic hydrogen  $\beta$ -anilidobenzylmalonate*,



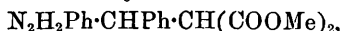
which melts at  $97.5^\circ$ , and easily decomposes with formation of benz-

aldehyde. With methylic benzylidenemalonate,  $\text{CHPh:C(COOMe)}_2$ , aniline unites to form *methylic  $\beta$ -anilidobenzylmalonate*,



which melts at  $117-118^\circ$ , and yields a very unstable *hydrochloride*.

Phenylhydrazine unites with methylic benzylidenemalonate yielding *methylic  $\beta$ -phenylhydrazidobenzylmalonate*,



which melts at  $94.5^\circ$ , and, when melted, or when boiled in absolute alcoholic solution, loses methylic malonate and forms benzylidene hydrazine,  $\text{N}_2\text{HPh} \cdot \text{CHPh}$ . The final result is thus a displacement of methylic malonate by phenylhydrazine, as W. Wislicenus has already pointed out (Abstr., 1894, i, 465).

Ethylic benzylidenemalonate reacts with aniline and with phenylhydrazine in the same way as does the methylic salt. C. F. B.

**Etherification of Aromatic Acids.** By VICTOR MEYER (*Ber.*, 1895, 28, 182—189).—The author has previously stated that hemimellitic acid,  $[\text{COOH}_3 = 1 : 2 : 3]$ , should only yield a diethylic salt on treatment with alcohol and hydrogen chloride. Graebe confirms this. Chloronitrobenzoic acid,  $[\text{COOH} : \text{NO}_2 : \text{Cl} = 1 : 2 : 6]$ , is prepared most readily from nitrotoluidine, which is first converted into chloronitrotoluene and the latter oxidised with nitric acid. The benzoic acid yields no methylic salt with hydrogen chloride and methylic alcohol; the rule applies therefore when the substituting groups are dissimilar.

Attempts to prepare an isomeric ethylic tetrachlorophthalate (compare this vol., i, 93) were unsuccessful. As previously surmised (*loc. cit.*), 2 : 1-chloronaphthalenecarboxylic acid gives no ethylic salt with alcohol and hydrogen chloride. 3 : 2-Chloronaphthalenecarboxylic acid, under similar circumstances, yields 90 per cent. of the ethylic salt; these results are contrasted with Jacobson's investigation of the formation of semidines (Abstr., 1893, i, 327).  $\gamma$ -Anthracenecarboxylic acid, as anticipated, gives no ethylic salt with alcohol and hydrogen chloride. Behla has previously shown that the same applies to  $\gamma$ -chloranthracene- $\gamma$ -carboxylic acid, and Börnstein that the isomeric acid readily yields an ethylic salt. Nitrotoluidine,  $[\text{Me} : \text{NO}_2 : \text{NH}_2 = 1 : 2 : 4]$ , was converted into the corresponding bromotoluic acid,  $[\text{Me} : \text{COOH} : \text{Br} = 1 : 2 : 4]$ , and this was found to be identical with Racine's acid (m. p.  $167^\circ$ ), to which he assigned the constitution  $[\text{Me} : \text{COOH} : \text{Br} = 1 : 2 : 3]$ , and which gives, as he states, an ethylic salt with alcohol and hydrogen chloride.

An investigation of the rate of etherification of hydroxycarboxylic acids is in progress. The acids in all cases were dissolved in methylic alcohol and treated with hydrogen chloride during eight hours, the solution being maintained at the following temperatures:  $-0^\circ$ ,  $20^\circ$ ,  $40^\circ$ , and the boiling point of methylic alcohol. Salicylic acid yields 9—10, 33—34, 81—82, and 98 per cent. of methylic salt respectively; hydroxynaphthalenecarboxylic acid  $[\text{COOH} : \text{OH} = 1 : 2]$  gives 0, 3, 26, and 63.5 per cent. respectively; the acid,  $[\text{COOH} : \text{OH} = 2 : 3]$ , yields, at ordinary temperatures, 90 per cent. of methylic salt. Para-

hydroxybenzoic acid reacts as readily as benzoic acid, the meta-compound rather more slowly. If the solution of salicylic acid is not cooled, 50 per cent. of methylic salt is formed in eight hours. Methylic hydroxynaphthalenecarboxylate,  $[\text{COOMe} : \text{OH} = 1 : 2]$ , dissolves in alkalis without colour, the 2 : 3 isomeric compound gives an intensely yellow solution. J. B. T.

**Action of Sulphuric acid on Charcoal.** By GIRAUD (*Bull. Soc. Chim.*, 1894, [3], 11, 389—391).—During the preparation of sulphurous anhydride from charcoal and sulphuric acid, a white, crystalline sublimate occasionally forms in the neck of the flask, and may be obtained in quantity by using excess of charcoal and carrying on the action until gas ceases to be evolved. After purification and recrystallisation from alcohol, this substance forms small, colourless, efflorescent crystals, which, on sublimation, are transformed into a substance crystallising in long needles and melting at  $280^{\circ}$ . This forms a phthalein with phenol and sulphuric acid, and is probably pyromellitic anhydride, the original substance being the corresponding acid. Mellitic acid is possibly the first product. The substances are formed by the oxidation of some hydrogenated carbon compound, as neither coke nor recently ignited charcoal yield any crystals. Sugar and cellulose give a very poor yield, but ordinary coal yields as much as 5 per cent. J. N. W.

**Unsaturated Sulphones: Allylphenylsulphone and Allylparatolylsulphone.** By ROBERT OTTO (*Annalen*, 1894, 283, 181—208; compare Abstr., 1891, 1067 and 1229).—Allylphenylsulphone,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{SO}_2\text{Ph}$ , is obtained by heating the alcoholic solution of sodium benzenesulphinate in a reflux apparatus with allylic bromide (1 mol.) until the odour of the latter is no longer perceptible; it is a yellowish, odourless oil, which is heavier than water and is not miscible with it.

Allylparatolylsulphone is prepared in a similar manner from sodium paratoluenesulphinate; it melts at  $52\text{--}53^{\circ}$ , and forms crystals which belong to the monosymmetric system,  $a : b : c = 1.6955 : 1 : 0.6671$ .  $\beta = 84^{\circ} 51'$ . Both sulphones are hydrolysed by alcoholic potash with formation of allylic alcohol and regeneration of the sulphinic acids from which they are derived; when reduced with zinc and hydrochloric acid, they give rise to the corresponding mercaptans.

$\alpha\beta$ -Dibromopropylphenylsulphone is obtained by the action of bromine on phenylallylsulphone; it forms small plates which melt at  $80^{\circ}$ .  $\alpha\beta$ -Dibromopropylparatolylsulphone melts at  $81\text{--}82^{\circ}$ . On heating the former compound for several days with water at  $110^{\circ}$ , hydrogen bromide is eliminated with formation of phenylsulphone- $\alpha$ -propylene glycol,  $\text{CH}_2(\text{OH})\cdot\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{SO}_2\text{Ph}$ , which crystallises in long, lustrous needles melting at  $135\text{--}136^{\circ}$ . The dibenzoyl derivative forms silky needles which melt at  $86\text{--}87^{\circ}$ ; it is obtained by the action of benzoic chloride on the glycol, and also by heating a mixture of silver benzoate and  $\alpha\beta$ -dibromopropylphenylsulphone at  $120^{\circ}$  in benzene.

When the alcoholic solution of sodium benzenesulphinate is heated with dichlorhydrin for eight days, an oil is formed which contains a

small quantity of symmetrical diphenylsulphonisopropyl alcohol (compare Otto and Rössing, Abstr., 1890, 780).

Dibromopropylphenylsulphone does not yield allylphenylsulphone when heated with molecular silver; it is decomposed into potassium benzenesulphinate and propargylic alcohol by the action of alcoholic potash. On heating the alcoholic solution with sodium benzenesulphinate (2 mols.) for some days, *biphenylsulphonepropane*,  $C_6H_5(SO_2Ph)_2$ , is formed, a small quantity of allyltriphenyltrisulphone being produced at the same time (compare E. Stuffer, Abstr., 1890, 987). This substance melts at  $101-102^\circ$ , and is probably geometrically isomeric with trimethylenediphenyldisulphone and propylenediphenyldisulphone, which melt at  $127-128^\circ$  and  $116^\circ$  respectively.

*Bitolylsulphonepropane*,  $C_6H_5(SO_2C_6H_4Me)_2$ , is formed when dibromopropyltolylsulphone is heated with sodium paratoluenesulphinate, a small quantity of allyltritolyltrisulphone being also produced; it melts at  $147-148^\circ$ , and is isomeric with trimethyleneditolylsulphone, which melts at  $124-128^\circ$ .

On heating a mixture of allylic tribromide and sodium benzenesulphinate in alcoholic solution, the corresponding trisulphone and a small quantity of biphenylsulphonepropane are formed. A similar reaction takes place between allylic tribromide and sodium paratoluenesulphinate.

*$\alpha$ -Dithiophenylpropylphenylsulphone*,



is obtained by heating the alcoholic solution of dibromopropylphenylsulphone with sodium phenylmercaptide on the water bath; it forms silky needles which melt at  $75-77^\circ$ . Oxidation with potassium permanganate converts it into allyltriphenyltrisulphone. On heating thiophenol (2 mols.) with epichlorhydrin, an oil is produced which yields the foregoing substance when heated with sodium benzenesulphinate; it therefore has the constitution  $SPh \cdot CH_2 \cdot CH(SPh) \cdot CH_2 \cdot Cl$ .

M. O. F.

**Iodo- and Iodoso-benzenesulphonic acids.** By A. C. LANGUIER (*Ber.*, 1895, 28, 90-96).—Pariodobenzenesulphonic chloride yields a yellow, crystalline *iododichloride*, which melts and decomposes at  $87-90^\circ$ , reacts readily with potassium iodide, and is somewhat unstable; when treated with soda, it yields sodium pariodobenzenesulphonate. As the sulphonic chloride is less soluble than iodobenzenesulphonic acid, it was better suited for this investigation. *Metiodobenzenesulphonic acid*, prepared from metasulphanilic acid, is extremely soluble; the sodium salt crystallises with  $1H_2O$  in colourless, lustrous plates. The *chloride*,  $C_6H_4I \cdot SO_2Cl$ , crystallises in long prisms, melting at  $23^\circ$ . The *sulphonamide* is deposited in lustrous needles or plates, and melts at  $152^\circ$ . The *iododichloride* resembles the para-compound; it melts and decomposes at  $87^\circ$ , and, with soda, yields sodium metiodobenzenesulphonate. The preparation of orthiodobenzenesulphonic acid is attended with great difficulty; it was converted into the chloride, and this into the *iododichloride*,  $ICl_2 \cdot C_6H_4 \cdot SO_2Cl$ , which is deposited in minute, pale yellow rhombohedra, and melts and decomposes at  $65-67^\circ$ . When acted on

by soda, it yields *sodium orthiodosobenzenesulphonate*,  $\text{IO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ ; it is a yellow, amorphous powder without smell, rapidly attacks potassium iodide solution in presence of acid, and yields iodobenzene-sulphonic chloride by the action of phosphorus pentachloride.

The three iodobenzenesulphonic acids resemble the corresponding iodobenzoic acids in the conditions under which they yield iodoso-derivatives.

The benzenesulphonic chlorides are reduced to thiophenols by boiling with potassium iodide solution. J. B. T.

**Dichloroxindenecarboxylic acid.** By THEODOR ZINCKE and M. ENGELHARDT (*Annalen*, 1894, **283**, 341—360; compare *Abstr.*, 1887, 54).— $\beta$ -Chloro- $\alpha$ -ketoindenecarboxylic acid,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{COOH}) \\ \text{CO} \end{array} \right\rangle \text{CCl}$ , is formed when dichloroxindenecarboxylic acid is heated with concentrated sulphuric acid at  $100\text{--}110^\circ$ . It crystallises in orange-red needles, and melts at  $224^\circ$ . The *methylic* salt forms brownish-yellow needles, which melt at  $105^\circ$ ; the *ethylic* salt melts at  $99\text{--}100^\circ$ , and gives rise to an *oxime*, melting at  $188^\circ$ . The *oxime* of the acid crystallises in dark yellow needles; it melts at  $256^\circ$ , and yields an *acetyl* derivative, which melts at  $218^\circ$ . Alkalis convert the acid into a *compound*,  $\text{C}_{20}\text{H}_{13}\text{ClO}_6$ , which melts at  $245^\circ$ . When chloroketoindenecarboxylic acid is reduced with sodium amalgam, it gives rise to an *acid*, which forms a *silver* salt and an *acetyl* derivative. Hypochlorous and hypobromous acids convert chloroketoindenecarboxylic acid into dichlorodiketohydrindene- and chlorobromodiketohydrindene-carboxylic acids respectively. When acted on by chlorine, it yields tetrachloroketohydrindene, whilst chlorodibromoketohydrindene-carboxylic acid,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CBr}(\text{COOH}) \\ \text{CO} \end{array} \right\rangle \text{CClBr}$ , is formed on treatment with bromine; this crystallises in white needles, and melts at  $171^\circ$ . The chlorobromo-derivative is decomposed by aqueous alkali, with formation of the *acid*  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CClBr}) \cdot \text{COOH}$ , which crystallises from hot water in needles, and melts at  $214^\circ$ . The *barium* salt contains  $1\text{H}_2\text{O}$ , and the *silver* salt is amorphous; the *dimethylic* salt melts at  $95^\circ$ .

The *lactone*,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{OH}) \\ \text{CCl} \end{array} \right\rangle \text{CCl}_2 \text{CO}$ , is obtained by the action of chlorine on dichloroxindenecarboxylic acid. It forms lustrous prisms, which melt at  $87^\circ$ , and is readily converted into dichloroketoindene with elimination of hydrogen chloride and carbonic anhydride. Dichloroketoxihydrindene-carboxylic acid is produced when the lactone is treated with aqueous sodium carbonate.

When the *methylic* salt of dichloroxindenecarboxylic acid is treated with chlorine, the *methylic* salt of tetrachloroxyhydrindene-carboxylic acid is formed; it melts at  $166^\circ$  (compare Zincke and Arust, *Abstr.*, 1892, 858). M. O. F.

**Synthesis of Indigo Blue.** By CARL ENGLER (*Ber.*, 1895, **28**, 309—312).—Twenty-five years ago the author and A. Emmerling synthetised indigo by heating syrupy nitracetophenone with a

mixture of zinc dust and soda-lime. Wichelhaus' failure to obtain indigo in this manner was probably due to the presence of metanitracetophenone in considerable quantity in the nitro-product, to the temperature being too high, or to the use of unsuitable zinc dust.

The following method of obtaining indigo is trustworthy, and may be employed as a lecture experiment. Zinc dust (24 grams), soda-lime (4 grams), and recently ignited marble (2 grams) are intimately mixed, orthonitracetophenone (1 gram) dissolved in chloroform (10 vols.) is added, and, after thorough stirring, the mixture is exposed to the air for 1—2 days; portions of 1 gram are heated in a test-tube blown to a bulb, and placed horizontally over the blow-pipe for seven seconds, or somewhat longer over a burner. The reaction is facilitated by filling the tube with hydrogen and passing the evolved gases through water; the result is even better if, to the orthonitracetophenone, an equal amount of acetophenone is added, and the mixture treated with zinc dust, &c., as above.

J. B. T.

**Synthesis of Quinizarin and Hystazarin.** By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 116—118).—When quinol dimethyl ether is heated with aluminium chloride and phthalic anhydride in presence of carbon bisulphide, 2:5-dimethoxyorthobenzoylbenzoic acid is formed. This crystallises in thick, white needles, melting at 162°, and by warming with concentrated sulphuric acid is converted into *quinizarin dimethyl ether*,  $C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_2(OMe)_2$ , which separates from alcohol in long needles, melting at 143°. From this compound, quinizarin can readily be obtained by hydrolysis with sulphuric acid.

Hystazarin may be prepared in a similar manner from veratroil. 3:4-Dimethoxyorthobenzoylbenzoic acid forms white, lustrous plates, melting at 233°. *Hystazarin dimethyl ether* crystallises from acetic acid in golden-yellow needles.

A. H.

**Constitution of Isomeric Symmetrical Di-derivatives of Diphenylmethane and of Benzophenone.** By WILHELM STAEDEL (*Annalen*, 1894, **283**, 149—151).—This paper contains a table setting forth the constitution of those dinitro-, diamido-, and dihydroxy-derivatives of diphenylmethane and of benzophenone, which are at present known.

M. O. F.

**Isomeric Dinitrodiphenylmethane Derivatives.** By WILHELM STAEDEL (*Annalen*, 1894, **283**, 151—164; compare *Abstr.*, 1894, i, 599).—Diphenylmethane when nitrated yields a mixture of 4:4'-dinitrodiphenylmethane, which melts at 183°, tetranitrodiphenylmethane, melting at 172°, and a small quantity of 2:4'-dinitrodiphenylmethane, which melts at 118°. After removal of these products, further nitration gives rise to *trinitrodiphenylmethane*, which melts at 109—110°; it is also obtained by heating diphenylmethane with fuming nitric acid (sp. gr. 1.53) for an hour at 50°.

4:4'-Diamidodiphenylmethane  $CH_2(C_6H_4 \cdot NH_2)_2$  ( $\alpha$ ), obtained by reducing the corresponding nitro-derivative with stannous chloride and hydrochloric acid, is identical with the base described by W. H.

Doer (this Journal, 1873, 170); it crystallises from hot water in lustrous plates, and melts at 85°. The *hydrochloride* and *sulphate* separate in well-formed crystals. The *diacetyl* derivative melts at 228°. The *diacetyl* derivative of 2 : 4'-diamidodiphenylmethane melts at 218—219°.

4 : 4'-Dihydroxydiphenylmethane is obtained from the amido-compound by means of the diazo-reaction; the *nitro*-derivative melts at 224°, and yields a *barium* salt, which separates in red crystals.

M. O. F.

**Dinitro-, Diamido-, and Dihydroxy-Derivatives of Benzophenone.** By WILHELM STAEDEL (*Annalen*, 1894, 283, 164—180).—This paper contains an account of the production of dinitro- from mononitro-derivatives of benzophenone, a summary of the results having already appeared (*Abstr.*, 1894, i, 599). The nitro-compounds give rise to the corresponding amido-derivatives on reduction.

4 : 2'-*Diamidobenzophenone* ( $\delta$ ) forms lustrous, straw-yellow needles, which melt at 128—129°; the *diacetyl* derivative crystallises in white plates, which melt at the same temperature, with evolution of gas. 2 : 3'-*Diamidobenzophenone* ( $\epsilon$ ) crystallises in golden-yellow plates, which melt at 80°; the *diacetyl* derivative is colourless, and melts at 167°. *Nitramidobenzophenone* is formed on reducing 2 : 3'-dinitrobenzophenone with tin and hydrochloric acid; it melts at 116°.

2 : 2'-Dihydroxybenzophenone is obtained from the amido-derivative by means of the diazo-reaction, xanthone being formed at the same time; it melts at 115°. 3 : 2'-Dihydroxybenzophenone is prepared in a similar manner; it forms white needles, which melt at 126°, instead of 121—122° as previously stated. A red, crystalline substance is also formed. The *acetyl* derivative of 3 : 2'-dihydroxybenzophenone melts at 154°.

2 : 4'-*Dihydroxybenzophenone*  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$  is identical with the substance obtained by A. Michael on heating a mixture of salicylic acid and phenol in presence of stannic chloride; the author has also prepared it from 2 : 4'-diamidobenzophenone by means of the diazo-reaction. It melts at 142°. The older method of preparation also gives rise to 4 : 4'-dihydroxybenzophenone, which melts at 210°. These two derivatives are formed when phenylic salicylate is heated with stannic chloride, but when phenylsalicylic acid is employed, the sole product is xanthone.

The dihydroxy-derivatives of benzophenone exhibit a certain regularity in their melting points.

M. O. F.

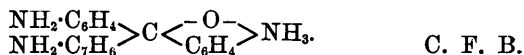
**Hydroxydiphenylene Ketones and Hydroxydiphenylcarboxylic acids.** By WILHELM STAEDEL (*Ber.*, 1895, 28, 111—113; compare this vol., i, 147, and preceding page).—The substance obtained from symmetrical diorthodiamidobenzophenone by diazotising, and boiling with water the diazo-salt produced, is a *hydroxydiphenylene ketone*. It melts at 115°, is intensely yellow, and forms a wine-red solution in concentrated sulphuric acid. When its potassium salt is brought into fused potash, a carmine-coloured mass is first obtained, which soon becomes colourless. This contains the potassium salt of *orthophenylsalicylic acid*,  $[\text{Ph} : \text{COOH} : \text{OH} = 1 : 2 : 3]$ , which crystallises from water in small prisms melting at

159°. It closely resembles salicylic acid in its properties, and, by treatment with strong sulphuric acid, is reconverted into the hydroxyphenylene ketone. Phenylbenzoic acid undergoes a similar reaction when dissolved in concentrated sulphuric acid.

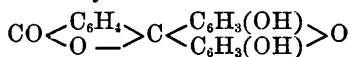
The product obtained, in addition to symmetrical orthometadihydroxybenzophenone, from symmetrical orthometadiamidobenzophenone, is also probably a hydroxyphenylene ketone. By fusion with potash, it is converted into an acid, which is probably *orthophenylmethahydroxybenzoic acid*. Both the hydroxyphenylene ketones are coloured substances, and moreover act as dyes. A. H.

**Constitution of the Triphenylmethane Colour-bases.** By HUGO WEIL (*Ber.*, 1895, 28, 205—215).—Reasons are given for supposing that compounds such as pararosaniline have the constitution  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_2\text{C} < \overset{\text{O}}{\text{C}_6\text{H}_4} > \text{NH}_2$ , rather than  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_3\text{C} \cdot \text{OH}$ , which is usually assigned to them, although they are stronger bases than the leuco-compounds, from which they are supposed to be derived by the displacement of H by OH, a change which should *lessen* the basic properties. In the first place, only *two* amido-groups in rosaniline react with paranitrobenzaldehyde, *dinitrodibenzylidenerosaniline*,  $\text{C}_{34}\text{H}_{22}\text{N}_5\text{O}_6$ , being formed, a yellow, crystalline substance melting at 235°; the same compound appears to be formed when rosaniline acetate is used. If, however, hydrocyanorosaniline, in which the CN group is known to be united to carbon, is used, a *trinitrotribenzylidenerosaniline* compound,  $\text{C}_{42}\text{H}_{23}\text{N}_7\text{O}_8$ , is formed; this is a yellow, crystalline powder, and melts at 144—145°. Secondly, the oxygen atom does not react like hydroxyl oxygen, but rather resembles that in ethylenic oxide and epichlorhydrin. Malachite green,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} < \overset{\text{O}}{\text{C}_6\text{H}_4} > \text{NHMe}_2$ , yields a colourless *oxime* and a yellowish *phenylhydrazone*, which melt and decompose at 168° and 167° respectively. And, lastly, malachite green, when heated at 200°, behaves very like tetramethylammonium hydroxide; it loses, not methylic alcohol, indeed, but formaldehyde, and there remains a brownish substance which melts at 155—156°, and may be either  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$  or  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} : \text{C}_6\text{H}_4 \cdot \text{NH}_2\text{Me}$ .

Attention is called to the fact that the new formula allows of two isomeric rosanilines,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_2\text{C} < \overset{\text{O}}{\text{C}_7\text{H}_6} > \text{NH}_2$  and

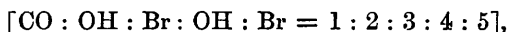


**Constitution of Fluoresceïn and Eosin.** By GUSTAV HELLER (*Ber.*, 1895, 28, 312—316).—Graebe's failure to obtain anthraquinone derivatives from dihydroxyorthobenzoylbenzoic acid or its ethereal salts has led him to suggest that the hydroxyl groups are not in the para-position relatively to the methane carbon atom, and that fluoresceïn is represented by the formula





[C : OH : O = 1 : 2 : 6]; the generally accepted constitution is [C : OH : O = 1 : 4 : 6] (compare this vol., i, 182). The author has also failed to obtain an anthraquinone derivative from hydroxyorthobenzoylbenzoic acid [CO : OH = 1 : 4] (Abstr., 1893, i, 274), whilst Nourisson prepared hydroxyanthraquinone from the corresponding methoxy-derivative. The reason for this difference is that in the former case a sulphonic acid is formed which is incapable of condensation; in the latter, the methoxyanthraquinone which is first produced is immediately hydrolysed. Dihydroxyorthobenzoylbenzoic acid yields a dibromo-derivative which is identical with Baeyer's "dibromomono-resorcinolphthalein," prepared by the action of soda on eosin; when heated with fuming sulphuric acid, it is converted into dibromodihydroxyanthraquinone [OH : Br : OH : Br = 1 : 2 : 3 : 4], Plath's "dibromoxanthopurpurin;" dibromodihydroxyorthobenzoylbenzoic acid must therefore have the constitution



since one of the hydroxyl groups (oxygen atom) in fluorescein is certainly in the ortho-position to the methane carbon atom. The position of the bromine atoms in eosin is also determined, since both in this compound and in fluorescein the resorcinol radicles are symmetrical.

Hydroxyorthobenzoylbenzoic acid also yields a dibromo-derivative which condenses in a manner similar to the dihydroxy-compound, forming the dibromohydroxyanthraquinone which Baeyer prepared by heating tetrabromophenolphthalein with concentrated sulphuric acid (Abstr., 1880, 654).

J. B. T.

**Nitronaphthalenes.** By WILHELM WILL (*Ber.*, 1895, 28, 367—379).—The substance melting at 212°, described by de Aguiar, and afterwards by Beilstein and Kuhlberg (*Annalen*, 169, 99), as  $\alpha$ -tetranitronaphthalene, is a mixture of two compounds, which may be separated by treatment with cold acetone.  $\gamma$ -Tetranitronaphthalene is readily soluble in acetone, and crystallises in pale yellow, lustrous tetrahedra melting at 194—195°. It dissolves without decomposition in concentrated nitric or sulphuric acid, but is decomposed by alkalis. When treated with phosphorus iodide and water, it is converted into the crystalline *hydriodide of  $\gamma$ -tetramidonaphthalene*, from which the free base has not as yet been prepared. When the nitro-compound is suspended in methylic alcohol and treated with a solution of sodium methoxide, *methylic  $\gamma$ -trinitronaphthyllic ether*,  $\text{C}_{10}\text{H}_4(\text{NO}_2)_3\text{OMe}$ , is formed. This substance crystallises in golden-yellow needles, and melts at 186°.  $\gamma$ -Tetranitronaphthalene is converted by oxidation with dilute nitric acid or sodium peroxide into paradinitrophthalic acid, melting at 201° [ $\text{NO}_2 : \text{COOH} : \text{COOH} : \text{NO}_2 = 1 : 2 : 3 : 4$ ]. The trinitronaphthyllic ether, on the other hand, is not oxidised by sodium peroxide, but is converted by nitric acid into metadinitrophthalic acid, melting at 226° [ $\text{NO}_2 : \text{COOH} : \text{COOH} : \text{NO}_2 = 1 : 2 : 3 : 5$ ]. The  $\gamma$ -compound is therefore a 1 : 3 : 1' : 4'-tetranitronaphthalene, and the substitution of methoxyl for the nitro-group takes place in agreement with the observations of Lobry

de Bruyn, according to which ortho- and para-nitro-groups are readily displaced, whilst meta-groups are not.

$\delta$ -Tetranitronaphthalene is insoluble in acetone and all the usual solvents. It may be recrystallised from boiling ethyl benzoate or concentrated nitric acid, and forms slender needles or compact prisms which begin to decompose at  $270^{\circ}$ , but do not melt even at  $310^{\circ}$ . Like the  $\gamma$ -compound, it can be reduced to a *tetramido-compound*, of which the *hydriodide* is a crystalline substance, easily decomposed by a large amount of water. The free base has not yet been isolated.  $\delta$ -Trinitronaphthyl methyl ether crystallises in yellow needles melting at  $191^{\circ}$ . On oxidation with sodium peroxide, the  $\delta$ -tetranitro-compound yields paradinitrophthalic acid (m. p.  $201^{\circ}$ ), whilst with nitric acid it gives an acid which is most probably paradinitrobenzoic acid. The trinitronaphthyl ether also yields paradinitrophthalic acid when treated with nitric acid. Since the  $\delta$ -compound is obtained by the nitration of 1:4'-dinitronaphthalene, it follows from the result of the above oxidation experiments that three of the nitro-groups must have the positions 1:4:4'. The position of the fourth follows from the constitution of the trinitronaphthalene, from which it can be prepared. Two trinitronaphthalenes derived from  $\alpha$ -dinitronaphthalene have hitherto been described. A third,  $\delta$ -trinitronaphthalene, is formed, along with the  $\alpha$ -trinitro-compound, when  $\alpha$ -dinitronaphthalene is heated with a large amount of nitric acid of sp. gr. 1.42. It crystallises from alcohol in slender, colourless needles melting at  $112$ – $113^{\circ}$ .

$\gamma$ -Trinitronaphthalene, melting at  $154^{\circ}$ , is converted by oxidation with nitric acid into paranitrophthalic acid, and with sodium peroxide into orthomononitrophthalic acid. It therefore has the constitution 1:4:4'. Fuming nitric acid and sulphuric acid convert it into a mixture of the  $\gamma$ - and  $\delta$ -tetranitro-compounds.  $\alpha$ -Trinitronaphthalene, on oxidation with sodium peroxide, yields orthomononitrophthalic acid, whilst on further nitration, it only gives the  $\gamma$ -tetranitro-compound.

The new  $\delta$ -trinitronaphthalene yields, on nitration, the  $\delta$ -tetranitro-compound, accompanied by another substance which has not been examined.

Since  $\gamma$ -tetranitronaphthalene (1:3:1':4') can only be obtained by the nitration of the trinitronaphthalenes 1:4:4' and 1:3:4' (both derived from 1:4'-dinitronaphthalene), and since  $\gamma$ -trinitronaphthalene has been shown to have the constitution 1:4:4', it follows that  $\alpha$ -trinitronaphthalene has the constitution 1:3:4'.  $\delta$ -Trinitronaphthalene must therefore be the 1:2:4'-compound, since 1:4'-dinitronaphthalene can only yield these three trinitro-derivatives.  $\delta$ -Tetranitronaphthalene, being formed by the nitration of both the  $\gamma$ - and the  $\delta$ -trinitro-compounds, must therefore have the constitution 1:2:1':4'.

$\gamma$ - and  $\delta$ -tetranitronaphthalene are formed in about equal amounts by the nitration of dinitronaphthalene, and are accompanied by paradinitrophthalic acid and another substance, melting at  $200^{\circ}$ , which has not been further examined.

$\beta$ -Dinitronaphthalene [1:1'] on nitration appears to yield only

one derivative,  $\beta$ -tetranitronaphthalene, a certain amount of meta-dinitrophthalic acid being also formed. This substance does not react with sodium methoxide, and is therefore probably the 1 : 3 : 1' : 3'-compound.

A. H.

**Thio-derivatives of  $\beta$ -Naphthol.** By ROBERT HENRIQUES (*Ber.*, 1895, 28, 114).—The author admits the identity of the substances previously described by him with those first prepared by Schiller-Wechsler (this vol., i, 150). The melting point of dehydrodihydroxydinaphthyl sulphide (thiodinaphthyl oxide) is  $155^{\circ}$  and not  $159$ – $160^{\circ}$  as stated by Schiller-Wechsler.

A. H.

**Derivatives of Iodohydroxynaphthaquinone (Iodonaphthalic acid).** By FRIEDRICH KEHRMANN and B. MASCIONI (*Ber.*, 1895, 28, 345–352).—Iodohydroxy- $\alpha$ -naphthaquinone is prepared by treating hydroxynaphthaquinone, dissolved in acetic acid, with sodium iodide and iodate in presence of sulphuric acid. It crystallises in thick, yellowish-brown, lustrous prisms, is almost insoluble in water, and melts and decomposes at above  $170^{\circ}$ . The alkali solutions are blood-red, and the sodium salt crystallises in dark red masses. The silver salt is a dark red, crystalline powder. The *methylic ether*, melting at  $156$ – $157^{\circ}$ , and the *ethylic ether*, melting at  $128$ – $129^{\circ}$ , form pale yellow needles. The silver salt is completely decomposed by water or dilute ammonia at  $120^{\circ}$ , no hydroxy- or amido-derivative being formed. Stannous chloride reduces the iodoquinone to 1 : 2 : 4-trihydroxynaphthalene, which is at once converted by the oxygen of the air into hydroxynaphthaquinone. The methylic ether, on reduction, yields colourless plates of *dihydroxymethoxyiodonaphthaquinone*, which cannot be isolated in the pure state. The corresponding *diacetate*,  $C_{10}H_4(OAc)_2(OMe)I$ , crystallises in thick, colourless prisms melting at  $162$ – $163^{\circ}$ . *Iodamidonaphthaquinone*,  $C_{10}H_4O_2(NH_2)I$ , is obtained by the action of alcoholic ammonia on the methylic ether, and forms dark red needles melting at  $192$ – $193^{\circ}$ . On reduction, it yields 2-amido-1 : 4-naphthaquinone, identical with that described by Meerson (*Abstr.*, 1888, 713, 1200). This method of preparation affords an independent proof of the constitution of the base. Iodohydroxynaphthaquinone combines with aniline to form a salt, which is at once decomposed by hydrochloric acid, but when heated with aniline in alcoholic solution it yields anilido- $\alpha$ -naphthaquinone. With orthophenylenediamine it yields  $\alpha$ -naphthoeurhodole, a portion of the diamine being also oxidised to diamidophenazine. Phenylphenylenediamine reacts in a similar manner, rosindone and the hydriodide of the oxidation product of the amine, which has been described by Fischer and Heiler (*Abstr.*, 1893, i, 266) being formed.

*Hydroxyiodonaphthaquinonoxime* crystallises with  $2H_2O$  in yellow prisms, which lose their water at  $100^{\circ}$  and decompose at  $160^{\circ}$  without melting. When reduced with stannous chloride, the oxime is converted into 1 : 2 : 4-*amidodihydroxynaphthalene*, the hydrochloride of which is precipitated by hydrochloric acid from aqueous solution in colourless crystals. Ferric chloride converts it into hydroxynaphthaquinone. The neutralised solution, when exposed to atmo-

spheric oxygen, yields naphthoresorufin (compare this vol., i, 246), whilst a strongly alkaline solution is thereby converted into hydroxynaphthaquinone.

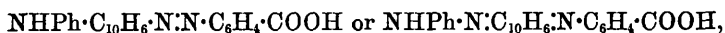
When the hydrochloride is treated with sodium acetate and acetic anhydride, the *triacetyl-derivative* is obtained in thick tablets melting at 155—156°. The base just described is identical with the product of reduction of hydroxynaphthoquinonoxime, and, since 1 : 3 : 4-amidodihydroxynaphthalene and 2 : 1 : 4-amidodihydroxynaphthalene are already known, must have the constitution of a 1 : 2 : 4-amidodihydroxynaphthalene, only these three isomerides, having the three groups in the positions 1 : 2 : 4, being possible. It hence follows that, by the action of alkaline hydroxylamine on hydroxynaphthaquinone and its iodo-derivative, the oxygen atom adjacent to the hydroxyl group is displaced.

A. H.

**Azo-derivatives of Phenyl- $\beta$ -naphthylamine.** By THEODOR ZINCKE (*Ber.*, 1895, 28, 328—333).—A general account is given of the ammonium base derived from benzenazo- $\beta$ -naphthylphenylamine (*Abstr.*, 1890, 990); the constitution of both compounds is discussed; and they are compared with the formazyl and tetrazolium derivatives respectively. Marshall's work is also summarised (following abstract).

J. B. T.

**Anilido- and Paratolylamido- $\beta$ -naphthaleneazobenzoic acids and their Oxidation Products.** By J. W. MARSHALL (*Ber.*, 1895, 28, 333—340).—*Anilido- $\beta$ -naphthaleneparazobenzoic acid*,

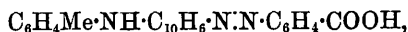


like its isomerides, is prepared from phenyl- $\beta$ -naphthylamine and diazobenzoic acid chloride in a manner similar to the benzene-derivative (*Abstr.*, 1887, 731). It is purified by means of the sodium salt, crystallises from glacial acetic acid in dark red, metallic, lustrous needles, and melts at 258°. The *sodium salt* crystallises in deep red plates, and is sparingly soluble in water. The *calcium* and *barium salts* and also those of the heavy metals are red to reddish-brown, and almost insoluble in water.

*Anilido- $\beta$ -naphthalenemetazobenzoic acid* crystallises in light red, lustrous needles, and melts at 235°. The *sodium salt* is deposited in light red plates; like the other salts, it resembles the *para-compound*.

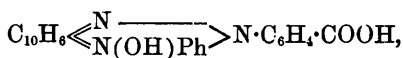
*Anilido- $\beta$ -naphthaleneorthazobenzoic acid*, like its salts, is more readily soluble than the meta- and para-compounds, it crystallises in red needles, and melts at 215°.

*Paratolylamido- $\beta$ -naphthaleneparazobenzoic acid*,



prepared like the phenyl derivative, forms small, dark red, crystalline granules or needles, is very sparingly soluble, and melts at 262°. The *sodium salt* crystallises in dark red, metallic, lustrous plates, and dissolves with difficulty. The salts of the other metals are insoluble

and red to brownish-red. The corresponding *meta*- and *ortho*-acids crystallise in red needles, resemble the phenyl derivatives, and melt at  $245^{\circ}$  and  $221^{\circ}$  respectively. The salts resemble those of the phenyl compounds. The above azo-compounds are all readily resolved into benzonaphthazine and tolunaphthazine when boiled with glacial acetic acid and a little hydrochloric acid. By the action of bromine in glacial acetic acid solution, bromobenzoic acids and tetrabromophenyl- or tetrabromotolyl- $\beta$ -naphthylamine are formed; the latter compound crystallises in slender, lustrous needles, and melts at  $168^{\circ}$ . The action of chlorine has only been studied in the case of anilido- $\beta$ -naphthaleneparazobenzoic acid, which yields diazobenzoic acid chloride and chloronaphthylphenylamine, the former only was isolated. The three benzoic acid phenyl compounds when oxidised yield ammonium bases,  $C_{10}H_6 \cdot \begin{smallmatrix} N \\ \text{---} \\ N(OH)Ph \end{smallmatrix} \geq N \cdot C_6H_4 \cdot COOH$  or



which easily form betaines,  $C_{10}H_6 \cdot \begin{smallmatrix} N \\ \text{---} \\ NPh \end{smallmatrix} > N \cdot C_6H_4 \cdot \text{---} O > CO$ ; these have an extremely bitter taste, become red on treatment with soda, regenerate the diazo-compounds when reduced, decompose when heated alone, and do not affect litmus paper. The *parabetaine* crystallises with  $3H_2O$  in highly lustrous prisms; its *chloride*,  $C_{23}H_{16}N_3O_2Cl$ , is deposited in pale yellow needles or plates, the *sulphate* in pale yellow, the *nitrate* in colourless needles. The *metabetaine* crystallises with  $3H_2O$  in thick, highly lustrous, yellowish needles; its *chloride* and *nitrate* are deposited in pale yellow needles. The *orthobetaine* is deposited in small, lustrous, monoclinic prisms with  $2H_2O$ . The salts crystallise with difficulty, the *chloride* in small plates, the *nitrate* in granules, and the *sulphate* in needles. All three betaines form *platinochlorides* which are yellow, and *mercurochlorides* which are white.

J. B. T.

**Derivatives of Naphthalic acid.** By GEORGE F. JAUBERT (*Ber.*, 1895, 28, 360—364).—The author has investigated a number of alkyl substitution products and other derivatives of naphthalimide. The *potassium* salt of naphthalimide,  $C_{10}H_6 \cdot (CO)_2 \cdot NK$ , crystallises in small, colourless needles, and the *sodium* salt closely resembles it. *Methylnaphthalimide* may be prepared by acting on the potassium salt with methylic iodide or by acting on naphthalic anhydride with methylamine. It forms small, white needles melting at  $205^{\circ}$ . *Ethyl-naphthalimide* also forms small needles, and melts at  $148^{\circ}$ . *Phenyl-naphthalimide* (naphthalanil), obtained by the direct action of aniline, also crystallises in small needles, and melts at  $202^{\circ}$ . *Orthotolyl-naphthalimide* melts at  $214.2^{\circ}$ . *Benzyl-naphthalimide* melts at  $196.6^{\circ}$ . *Naphthaloxime* (naphthalhydroxamic acid),  $C_{10}H_6 \cdot (CO)_2 \cdot N \cdot OH$ , is prepared by the action of hydroxylamine in alkaline solution on the anhydride. It forms a white, matted, crystalline mass, and melts at  $284^{\circ}$ . It readily forms metallic salts which are coloured red, the *potassium*, *sodium*, and *silver* salts having been analysed. *Methyl-*

*naphthaloxime*, like the oxime itself, is colourless, and melts at  $212^{\circ}$ . *Ethyl-naphthaloxime* forms small needles melting at  $160^{\circ}$ . *Naphthal-phenylhydrazone*,  $C_{10}H_6:(CO)_2:N \cdot NPh$ , is obtained by the direct action of phenylhydrazine on the anhydride at  $170^{\circ}$ ; it crystallises in compact prisms melting at  $218.5^{\circ}$ . Acetic chloride converts it into the *acetyl* derivative, which forms small, white plates, and melts at  $230^{\circ}$ .

*Benzoylnaphthalphenylhydrazone* crystallises in small needles, and melts at  $235^{\circ}$ . Naphthalphenylhydrazone is converted, by reduction, into a substance which is apparently the *hydrazone* of *hydroxynaphthalide*,  $C_{10}H_6 < \begin{smallmatrix} C(OH)H \\ \text{---} CO \text{---} \end{smallmatrix} > N \cdot NPh$ , since, on distillation, it decomposes into naphthalimide and aniline.

A. H.

**Campholenes and the Constitution of Camphor.** By AUGUSTE BÉHAL (*Compt. rend.*, 1894, **119**, 858—862).—The campholene obtained by the action of heat on the campholenic acid previously described (next page) boils at  $135.5^{\circ}$  under a pressure of 755 mm., is optically inactive, and has an odour of terebenthene; sp. gr. at  $0^{\circ} = 0.8134$ . It combines with hydrogen iodide with development of heat, and the crystalline compound formed melts at about  $61^{\circ}$ ; this is very unstable, losing hydrogen iodide gradually when exposed to the air, and instantly in presence of water. When treated with an alkali, it yields *isocampholene*, an isomeride of the original hydrocarbon, which boils at  $134^{\circ}$ ; sp. gr. at  $0^{\circ} = 0.8117$ . Isocampholene yields the original compound with hydrogen iodide, and is identical with the campholene obtained by Guerbet from campholic acid.

The existence of two campholenes throws some light on the position of the ethylene linking in campholene. The action of bromine on campholene and isocampholene in presence of dry chloroform gave no definite results, 4 atoms of bromine being taken up. Nitrosyl chloride, on the other hand, yields a blue crystalline product with isocampholene, but not with campholene, and hence it would seem that in isocampholene the ethylene linking is in the nucleus and in campholene in the side chain. This view agrees with the behaviour of the hydriodide and the formation of isocampholene from the hydriodide produced by the campholene.

It is probable that in campholenic acid the carboxylic group is attached to the methylene group. This view is supported by the ready decomposition of the acid, the formation of a lactone boiling at  $255^{\circ}$  under a pressure of 760 mm., and the general chemical behaviour of camphor, which in the author's opinion has the constitution represented by Bouveault's formula.

C. H. B.

**Campholic acid.** By GUERBET (*Bull. Soc. Chim.*, 1894, [3], **11**, 426—433).—An improved method of preparing campholic acid is to heat camphor (500 grams) with sodium (40 grams) in xylene solution (500 c.c.), first at ordinary temperatures until the sodium has dissolved, and then, after removal of the solvent, &c., under low pressure in closed vessels for 24 hours at  $280$ — $290^{\circ}$ . The portion of the product soluble in water is neutralised with hydrochloric acid, and

the campholic acid precipitated by carbonic anhydride; after recrystallisation from alcohol it is pure.

Montgolfier's explanation of the mechanism of the action is incorrect, as the terpene, assumed by him to be formed, could not be detected.

Campholic acid is reduced by hydriodic acid to mesitylene, hexahydromesitylene, and pseudocumene. Hexahydromesitylene yields trinitromesitylene when nitrated in the usual manner. JN. W.

**Campholenic acids and Campholenamides.** By AUGUSTE BÉHAL (*Compt. rend.*, 1894, 119, 799—802).—When campholenonitrile, obtained by the action of acetic chloride on camphoroxime, and boiling at  $222^{\circ}$ , is boiled for about 20 minutes with alcoholic potash, it yields campholenamide, which crystallises from water or alcohol in silky needles melting at  $83^{\circ}$ . The melting point of this amide is generally stated to be between  $124^{\circ}$  and  $127^{\circ}$ .

When the amide is boiled for a long time with alcoholic potash, it yields campholenic acid, which is colourless, odourless, and tasteless, melts at  $50^{\circ}$ , and boils at  $185^{\circ}$  under a pressure of 120 mm. When quite pure, it also boils without change at  $247$ — $248^{\circ}$  under normal pressure, but in presence of a trace of alkali it completely decomposes into campholene and carbonic anhydride.

Although only slightly soluble in water, this campholenic acid is acid to litmus, and decomposes carbonates; its amide is hydrolysed without difficulty; when treated with hydrochloric acid and alcohol, it yields an ethylic salt which boils at  $225^{\circ}$ , and is rapidly hydrolysed by alcoholic potash, regenerating the original acid. These facts and the loss of carbonic anhydride on distillation all go to prove the existence of a true acid function. The acid also contains ethylenic carbon, for, when treated with hydrogen iodide in presence of light petroleum, it yields a crystalline acid which melts at  $66^{\circ}$  and decomposes in moist air, with liberation of hydrogen iodide and formation of an acid which is not identical with the original acid.

Campholenonitrile, dissolved in benzene, combines with hydrogen iodide with development of heat and formation of a white compound which melts at about  $84^{\circ}$ . It follows that the rupture of the camphor nucleus takes place at the moment of formation of the nitrile. This rupture can be brought about by most dehydrating agents. The compound of the nitrile with hydrogen iodide loses the latter more slowly under the influence of moist air and alkalis than the analogous compound formed by campholenic acid, and the nitrile formed is not identical with the original nitrile, although it has a similar odour and boils at nearly the same temperature. The former is slowly acted on by alcoholic potash, and yields an amide melting at  $92^{\circ}$ , whilst the former is rapidly attacked, and the amide melts at  $83^{\circ}$ .

Both amides have, however, very similar properties; they are only slightly soluble in water, and crystallise in needles very soluble in strong alcohol, but only slightly so in dilute alcohol of  $40^{\circ}$ . They are very soluble in hot, light petroleum, but only slightly in the cold.

It would seem that there are at least three distinct campholenic acids, the amides of which melt at  $83^{\circ}$ ,  $92^{\circ}$ , and  $127^{\circ}$  respectively.

C. H. B.

**Camphoronic acid: a Correction.** By OSSIAN ASCHAN (*Ber.*, 1895, 28, 224).—It was erroneously stated (this vol., i, 188) that the barium salt of *i*-camphoronic acid, unlike the two isomeric salts, is soluble in water. It is of the *calcium* salt that this is true; the barium salts of all three isomeric acids are only sparingly soluble in water. C. F. B.

**Camphoronic acid.** By JULIUS BREDT (*Ber.*, 1895, 28, 316—321).—*Anhydrocamphoronic chloride*,  $\text{O}:(\text{CO})_2:\text{C}_6\text{H}_{11}\cdot\text{COCl}$ , exists in two modifications; the  $\alpha$ -compound (m. p.  $131^\circ$ ) has been described by Kachler; it boils at  $164\text{--}165^\circ$  (13 mm.), and is then almost entirely converted into the  $\beta$ -compound which forms rhombic crystals, melts at  $38\text{--}39^\circ$ , and boils at  $151^\circ$  (10 mm.). *Methylic camphoronate*,  $\text{C}_6\text{H}_{11}(\text{COOMe})_3$ , boils at  $155^\circ$  (12 mm.). The *dimethylic salt* is formed together with the preceding compound, or from the anhydro-chloride. *Methylic anhydrocamphoronate*,



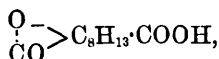
prepared by submitting the preceding compound to distillation, or from the anhydro-chloride, exists in two isomeric forms. The  $\alpha$ -compound is deposited in rhombic crystals, melts at  $138^\circ$ , and boils at  $166\text{--}167^\circ$  (12 mm.). The  $\beta$ -derivative forms similar crystals, is more soluble, melts at  $45^\circ$ , and boils at  $156^\circ$  (10 mm.). *Methylic dihydrogen camphoronate*,  $\text{C}_6\text{H}_{11}(\text{COOH})_2\text{COOMe}$ , obtained by the action of water on the preceding compound at ordinary temperatures, crystallises in needles melting at  $125\text{--}126^\circ$ .

*Anhydrocamphoronic anilide*,  $\text{O}:(\text{CO})_2:\text{C}_6\text{H}_{11}\cdot\text{CO}\cdot\text{NHPh}$ , is prepared from either of the anhydro-chlorides; it is crystalline and melts at  $202\text{--}203^\circ$ .

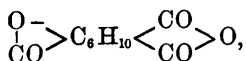
*Bromanhydrocamphoronic chloride*,  $\text{O}:(\text{CO})_2:\text{C}_6\text{H}_{10}\text{Br}\cdot\text{COCl}$ , formed by the interaction of bromine and either of the anhydrochlorides at  $120^\circ$ , is deposited from ether in monoclinic crystals, melts at  $168^\circ$ , and, when boiled with water, is converted into Kachler's " $\alpha$ -hydroxycamphoronic acid;" no  $\beta$ -compound could be detected. A second bromochloride is formed with the preceding compound, but on account of its ready solubility it could not be isolated; with water, it yields both  $\alpha$ - and  $\beta$ -hydroxycamphoronic acid. *Bromanhydrocamphoronic acid*,  $\text{O}:(\text{CO})_2:\text{C}_6\text{H}_{10}\text{Br}\cdot\text{COOH}$ , is prepared from the corresponding chloride (m. p.  $168^\circ$ ) by the action of glacial acetic acid; it is crystalline, and melts at  $154^\circ$ . A *methylic salt*,  $\text{O}:(\text{CO})_2:\text{C}_6\text{H}_{10}\text{Br}\cdot\text{COOMe}$ , is formed on boiling the bromochloride with methylic alcohol and rapidly cooling the solution; it is deposited in lustrous plates and in rhombic crystals, melts at  $100^\circ$ , and boils at  $177^\circ$  (15 mm.). By the action of hydrogen chloride in methylic alcoholic solution, an isomeric salt is formed which is deposited in rhombic crystals, melts at  $142^\circ$ , and, when boiled under reduced pressure, is resolved into methylic bromide, and Kachler's " $\alpha$ -hydroxycamphoronic anhydride;" it behaves, therefore, like a  $\gamma$ -bromo-ethylic salt. " $\alpha$ -Hydroxycamphoronic acid,"

$\begin{array}{c} \text{O} \\ \diagup \\ \text{CO} \end{array} > \text{C}_6\text{H}_{10}(\text{COOH})_2$ , is dibasic, and bears the same relationship to bromanhydrocamphoronic acid that camphanic acid,





does to bromocamphoric anhydride,  $\text{C}_8\text{H}_{13}\text{Br}(\text{CO})_2\text{O}$ ; it is the lactone of the  $\beta$ -hydroxy acid, and is formed from bromanhydrocamphoronic acid (see above) and water; the author suggests for it the name *camphoranic acid*. " $\beta$ -Hydroxycamphoronic acid,"  $\text{OH}\cdot\text{C}_6\text{H}_{10}(\text{COOH})_3$ , is tribasic; it may be converted into the lactone, and, when distilled, yields *camphoranic anhydride*,



which melts at  $136\text{--}137^\circ$ , and boils at  $175^\circ$  (10 mm.). *Dimethylic camphoranate*,  $\begin{array}{c} \text{O} \\ | \\ \text{CO} \end{array} > \text{C}_6\text{H}_{10}(\text{COOMe})_2$ , is deposited from water in long needles, from methylic alcohol in rhombic crystals, melts at  $111^\circ$ , and is formed in small quantity from methylic alcohol and bromanhydrocamphoronic chloride. The *methylic hydrogen salt*, formed together with the preceding compound, is deposited from water in rhombic spenoidal crystals with  $1\text{H}_2\text{O}$  and melts at  $81\text{--}83^\circ$ . The anhydrous compound melts at  $183^\circ$ , and is deposited from ether in tetragonal crystals. Most of the preceding compounds have been examined crystallographically; an account of the results, together with certain theoretical conclusions, will be given later. J. B. T.

**Some Points in Stereochemistry.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1894, [3], 11, 356—359).—A rejoinder to Combes (this vol., i, 108). The author maintains that it is possible for the four valencies of a carbon atom to exist in one plane, and that, moreover, when three of the valencies are in one plane, as in the central carbon atom of the author's formula for terebenthene, the fourth is necessarily also in the same plane. JN. W.

**Stereochemistry.** By ALPHONSE COMBES (*Bull. Soc. Chim.*, 1894, [3], 11, 436—439).—A reply to Bouveault (preceding abstract). JN. W.

**Essence of Ylang-ylang.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1894, [3], 11, 407—412).—There are two varieties of this essence, *oleum Anonæ odoratissimæ* and *oleum Canangæ*; the present paper refers to the former; this, when distilled under reduced pressure, is resolved chiefly into two fractions, the one boiling at  $100\text{--}112^\circ$ , the other at  $130\text{--}146^\circ$ .

The more volatile fraction is hydrolysed by alcoholic potash into benzoic acid and a phenol on the one hand, and an unsaturated isomeride of geraniol on the other. *Ylangol*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , the isomeride of geraniol (molecular weight by cryoscopic method), boils under 28 mm. pressure at  $103\text{--}107^\circ$ ; the sp. gr. =  $0.886$  at  $15^\circ$ ; the sp. rotatory power in alcoholic solution  $[\alpha]_D = -20.7^\circ$ . The refractive index at  $15.5^\circ$  is  $[\mu]_D = 1.472$ , and the molecular refractive power therefore  $48.64$ , a number pointing to the presence of two ethylene linkings in the molecule, and confirmed by the relative amount of iodine absorbed. *Ylangol*

is oxidised by chromic mixture to an aldehydic substance, probably citral.

The fraction boiling at 130—146° consists probably of a sesquiterpene. The author is proceeding with the study of the Cananga essence. JN. W.

**Constitution of Ring Systems.** By WILLY MARCKWALD (*Ber.*, 1895, 28, 114—116; compare *Abstr.*, 1894, ii, 474).—The author defends the conclusions as to the effect of reduction on the properties of various ring-compounds, given in his previous papers, against the criticism to which they have been subjected by Bamberger (*Ber.*, 27, 3427). A. H.

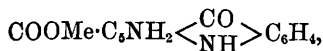
**Quinoline Bases in Brown Coal-tar.** By OSCAR G. DOEBNER (*Ber.*, 1895, 28, 106—107).—The fraction of brown coal-tar which boils between 220—280° contains quinoline and some of its homologues. The quinoline may be isolated by the recrystallisation of the picrates prepared from the redistilled fractions of this portion of the oil. The homologues have not yet been individually separated. A. H.

**Derivatives of  $\alpha$ -Quinoquinoline.** By ARNOLD REISSERT (*Ber.*, 1895, 28, 119—129).—The name quinoquinoline is ascribed to a (hypothetical) compound of the formula

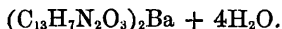
$$\begin{array}{c} \text{CH:CH}\cdot\text{C}\cdot\text{CH} \\ | \quad | \\ \text{CH:N}-\text{C}\cdot\text{N}- \end{array} > \text{C}_6\text{H}_4.$$

*Methyl chloronicotinate*  $\text{COOMe}:\text{Cl} = 3:6$  is prepared by acting with phosphorus pentachloride on the corresponding hydroxy-acid, and pouring the liquid thus obtained into methylic alcohol. It forms stellate groups of broad, lustrous needles and melts at 86—89°. It has a strong odour of fennel. *Ethoxynicotinic acid*,  $[\text{COOH}:\text{OEt} = 3:6]$ , is prepared by boiling chloronicotinic acid or its methylic salt with alcoholic soda. It forms small crystals melting at 183°.

Methylic chloronicotinate readily undergoes condensation with anthranilic acid when the two are heated together at 170°. The product consists of *methylic  $\alpha$ -quinoquinolone- $\beta$ -carboxylate*,



which crystallises in clusters of small, bright yellow needles, melting at 176°. It dissolves readily in mineral acids, forming salts which are not decomposed by water. Aqueous alkalis convert it into the acid, which can also be obtained by the direct condensation of the chloronicotinic acid with anthranilic acid.  *$\alpha$ -Quinoquinolone- $\beta$ -carboxylic acid* crystallises in small, soft, pale yellow needles, which melt and decompose at 318—319°. The freshly precipitated acid readily dissolves in mineral acids, whereas the crystalline acid only dissolves very slowly. The crystalline *barium* salt has the composition



The product of the direct condensation of chloronicotinic acid with anthranilic acid contains, in addition to the acid just described, a

compound which is probably  $\alpha$ -quinoquinolone- $\beta$ -carboxyorthocarboxyanilide,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_5\text{NH}_2 < \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$ .

This substance is sparingly soluble in cold ammonia and is precipitated by acids as a yellow, non-crystalline mass, which is almost insoluble in the usual solvents, but dissolves in concentrated nitric or sulphuric acid and is re-precipitated by the addition of water. It melts at  $336^\circ$ . When boiled with aqueous soda, it is converted into anthranilic acid and quinoquinolonecarboxylic acid.

$\alpha$ -Quinoquinolone,  $\text{C}_5\text{NH}_3 < \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$ , is formed when quinoquinolonecarboxylic acid is heated above its melting point. It crystallises in light yellow, lustrous needles, melting at  $210^\circ$ , and has strongly marked basic properties. Mineral acids dissolve it to form solutions which have a strong blue fluorescence. The *hydrochloride* forms light yellow needles melting at  $292$ – $293^\circ$ . The *platinochloride* melts at  $248^\circ$ , the *aurochloride* at  $236^\circ$  and the *picrate* at  $238^\circ$ . Quinoquinolone is not affected by distillation over heated zinc dust, by treatment with phosphorus pentachloride or by the action of sodium amalgam on its alcoholic solution. Hydriodic acid at  $220$ – $230^\circ$  converts it into a substance which crystallises in colourless, lustrous plates or broad needles, and melts at  $160^\circ$ ; this is probably *dibenzoyloctohydro- $\alpha$ -quinoquinoline*,  $\text{C}_5\text{NH}_3\text{Bz} < \begin{smallmatrix} \text{CH}_2 \\ \text{NBz} \end{smallmatrix} > \text{C}_6\text{H}_4$ .

A. H.

**Oxazines of the Naphthalene Series.** By FRIEDRICH KEHRMANN (Ber., 1895, 28, 353–359; compare Abstr., 1894, i, 54).—*Naphthophenoxazone*,  $\text{C}_{10}\text{H}_5\text{O} < \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_4$ , is formed when orthamidophenol is heated with hydroxynaphthaquinone in presence of 80 per cent. acetic acid. It crystallises from benzene in red, lustrous prisms and melts at  $191$ – $192^\circ$ . Nitric acid converts it into a *mononitro-derivative*, which crystallises in yellowish-brown needles and melts at  $232^\circ$ . When the preparation of naphthophenoxazone is carried out in alcoholic solution, the *ortho-hydroxyanilide*,  $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is formed; this is insoluble in benzene, and crystallises from alcohol in red needles melting at  $187$ – $188^\circ$ . *Chloronaphthophenoxazone*, prepared from chlorohydroxynaphthaquinone, crystallises in yellowish-red needles melting at  $194$ – $195^\circ$ .

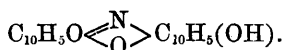
*Naphthophenoxazime*,  $\text{NH} \cdot \text{C}_{10}\text{H}_5 < \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} > \text{C}_6\text{H}_4$ , is obtained by the condensation of orthamidophenol with hydroxynaphthaquinonimide. It crystallises from nitrobenzene in reddish-brown plates with a metallic lustre, and melts at  $242$ – $243^\circ$ . When boiled with acetic acid, it is converted into naphthophenoxazone.

Benzoylorthophenylenediamine readily reacts with the naphthaquinones to form substances which are most probably anilides.

The *naphthaquinone benzoylamido-anilide*,  $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHBz}$ , crystallises in lustrous, yellowish-red needles and melts at  $238$ – $239^\circ$ . In alcoholic soda, it forms a violet solution which becomes blood-red when boiled, and then contains the sodium compound of  $\alpha$ -naphtho-

eurhodole, formed by the removal of the benzoyl-group, followed by condensation. The corresponding *anilide* from chlorodihydroxynaphthaquinone crystallises in lustrous tablets melting at  $237^{\circ}$ , and resembles the compound just described in its properties.

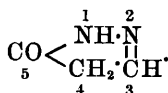
*Naphthoresorufin* is obtained by dissolving the hydrochloride of 1 : 2 : 4-amidodihydroxynaphthalene (compare this vol., i, 237) in water, along with an excess of sodium acetate and passing air through the liquid. A pale yellow precipitate is first produced which soon becomes dark coloured. The free base, isolated from the acetyl derivative, crystallises in dark red needles with a greenish lustre, and forms carmine coloured solutions with a fiery red fluorescence. Acids readily convert it into salts, and on heating with sulphuric acid, a *sulphonic acid* is produced, the alkali salts of which are blue and readily soluble in water, their solutions having an intense red fluorescence. The *acetyl* derivative crystallises from toluene in alizarin-red needles. It is probable that in the preparation of naphthoresorufin, the pale yellow precipitate which is first formed consists of an isomeric hydroxynaphthaquinonimide and that this then reacts with a molecule of the unoxidised base to form dinaphthoresorufin, which is therefore hydroxydinaphthoxazone,



A. H.

### Derivatives of Hydrazine having a Closed-chain Structure.

By THEODOR CURTIUS (*J. pr. Chem.*, 1894, [2], 50, 508—530; compare Abstr., 1893, i, 299).—The orientation of the pyrazolone derivatives dealt with in this paper is expressed by the enumeration,



3-Methylpyrazolone has been already described (Abstr., 1889, 393); it forms salts with both acids and bases, but these are of little stability.

1 : 3-Acetylmethylpyrazolone,  $\text{C}_4\text{N}_2\text{H}_5\text{AcO}$ , is the sole product of the action of acetic anhydride on 3-methylpyrazolone; it crystallises in colourless needles, melts at  $140^{\circ}$ , and is insoluble in ether and benzene but slightly soluble in alcohol and water; it behaves as a feeble acid, giving a colourless silver salt.

4 : 3-Isonitrosomethylpyrazolone,  $\text{OH} \cdot \text{N} \cdot \text{C}_4\text{N}_2\text{H}_4\text{O}$ , obtained by the action of nitrous acid on 3-methylpyrazolone, crystallises in yellow needles, melts at  $194^{\circ}$ , and dissolves somewhat easily in cold water and in alcohol. It behaves as a powerful acid and yields a *silver salt*; this crystallises in dark red needles, and reacts with ethylic iodide at  $115$ — $120^{\circ}$  forming the corresponding *ethylic* salt, which crystallises in yellow needles.

4 : 3-Benzylidenemethylpyrazolone,  $\text{CHPh} \cdot \text{C}_4\text{N}_2\text{H}_4\text{O}$ , is prepared by heating a mixture of the pyrazolone with benzaldehyde in molecular proportion, and crystallising the product from alcohol; it is a brick-red, crystalline powder, melts at  $204^{\circ}$  and is insoluble in water.

3-*Phenylpyrazolone*,  $C_9N_2H_3PhO$ , is prepared by warming a mixture of hydrazine hydrate (13 grams) and ethylic benzoylacetate (50 grams) in alcohol (150 grams), and subsequently cooling. It crystallises in thick, colourless prisms, melts and decomposes at  $236^\circ$ , and is nearly insoluble in cold alcohol, ether or benzene. It gives sparingly soluble precipitates in solutions of salts of the heavy metals. The *hydrochloride*,  $C_9N_2H_5O.HCl$ , crystallises in silky needles and melts and decomposes at  $195^\circ$ ; it dissociates when exposed to the air. 1:3-*Acetylphenylpyrazolone*,  $C_9N_2H_7AcO$ , crystallises in thick, colourless prisms, melts at  $121^\circ$ , and is sparingly soluble. 4:3-*Isonitrosophenylpyrazolone* crystallises in long, yellow needles, and gives a yellow, insoluble, silver salt.

Ethylic 3:4-*methylpyrazoloneacetate*,  $C_3N_2H_2MeO.CH_2.COOEt$ , is prepared by adding hydrazine hydrate (3.5 grams) to ethylic aceto-succinate (15 grams), diluted with an equal quantity of absolute alcohol, and warming. It crystallises in silvery laminæ, and large, colourless tables, melts at  $166^\circ$ , and dissolves in hot water and hot alcohol, but only sparingly in benzene or ether.

4-*Bis-3-methylpyrazolone*,  $NH < \begin{smallmatrix} N=CMe & MeC=N \\ CO \cdot CH & - HC \cdot CO \end{smallmatrix} > NH$ , is the product obtained when ethylic diacetosuccinate (1 mol.) reacts with hydrazine hydrate (2 mols.) in alcohol; it crystallises in minute, snow-white tablets, decomposes at  $250^\circ$ , and is sparingly soluble; dilute acids decompose it, hydrazine being separated, but it is very stable in the presence of alkalis; it reduces ammoniacal silver solution, but not Fehling's solution; aqueous ferric chloride colours it violet.

When ethylic diacetosuccinate and hydrazine hydrate, in molecular proportion, are heated together in alcohol, a compound which crystallises in colourless needles and melts at  $68-69^\circ$  is obtained. This can be distilled unchanged at 35 mm. pressure; it is insoluble in water, but dissolves easily in hot alcohol; dilute sulphuric acid separates hydrazine from it. Fehling's solution is not altered by it; silver nitrate gives a dirty yellow precipitate. The formula and constitution of the compound are only matter of conjecture at present.

*Levulinic hydrazide*,  $COMe.CH_2.CH_2.CO.NH.NH_2$ , is prepared by gently warming ethylic levulinate, diluted with an equal volume of alcohol, with hydrazine hydrate, in molecular proportion; on cooling, the new compound separates in the form of lustrous, colourless laminæ. It crystallises from water in large, colourless prisms, melts at  $82^\circ$  and dissolves in cold water and alcohol. The aqueous solution is neutral, gives no precipitate with benzaldehyde, and does not reduce mercuric oxide or Fehling's solution. It dissolves in both acids and alkalis, yielding hydrazine when warmed with the former. The hydrazide very readily loses a molecule of water, becoming the *anhydride*,

3-*methylpyridazinone*\*,  $CMe < \begin{smallmatrix} 2 & 1 \\ N & - NH \\ 3 & CH_2 \cdot CH_2 & 6 \\ & 4 & 5 \end{smallmatrix} > CO$ , which crystallises from

\* Previously called 3-methylpyridazolone (*Ber.*, 1893, 26, 408).

benzene in nacreous laminae, melts at  $94^{\circ}$ , and can be distilled at the ordinary pressure; it yields an isonitroso-derivative with nitrous acid, and is decomposed by hot dilute sulphuric acid, with separation of hydrazine.

*Ethyllic 3-phenylpyridazinone-5-carboxylate*,  $C_4N_2H_4PhO \cdot COOEt$ , is formed when ethylic  $\beta$ -benzoylisosuccinate and hydrazine hydrate in molecular proportion are mixed in well cooled alcohol; it crystallises in long, silky, colourless needles, melts at  $156^{\circ}$ , and dissolves in alcohol and hot water. It yields hydrazine when heated with dilute sulphuric acid, but it does not reduce Fehling's solution. The corresponding acid is a colourless, crystalline powder, which melts at  $116$ — $117^{\circ}$ , dissolves freely in hot water, and has a strong acid reaction. The *hydrazide* of the acid is obtained by heating the ethylic salt with hydrazine hydrate; it crystallises in long, colourless prisms, decomposes at  $190^{\circ}$ , and dissolves in hot water and alcohol; it reduces Fehling's solution, yields hydrazine hydrate when treated with alkalis, and gives a condensation product with benzaldehyde.

*3-Phenylpyridazinone*,  $C_4N_2H_5PhO$ , from methylic  $\beta$ -benzoylpropionate and hydrazine hydrate, crystallises in colourless prisms and needles, melts at  $149$ — $150^{\circ}$ , and is sparingly soluble in cold solvents. It is neutral and is decomposed with difficulty by hot dilute sulphuric acid, yielding hydrazine; it does not reduce Fehling's solution.

A. G. B.

**Pyrazoline and its Derivatives.** By THEODOR CURTIUS and F. WIRSING (*J. pr. Chem.*, 1894, [2], 50, 531—554; compare Abstr., 1893,

299).—*Pyrazoline*, 
$$\begin{array}{c} \text{NH} \\ \text{1} \quad \quad \quad \text{5} \quad \quad \quad \text{4} \\ \quad \quad \quad \text{CH}_2 \cdot \text{CH}_2 \\ \quad \quad \quad | \\ \text{2} \quad \quad \quad \text{3} \\ \quad \quad \quad \text{N} = \text{CH} \end{array}$$
, is best prepared by dissolving

acetaldehyde in three times its weight of ether, cooling, and dropping in rather more than the calculated quantity of hydrazine hydrate. The lower aqueous layer is saturated with hydrochloric acid, and evaporated at  $70^{\circ}$  until the bulk of the hydrazine has separated as dichloride; on further evaporation over caustic potash, the pyrazoline hydrochloride crystallises. This is purified by washing with strong alcohol, crystallisation from water, and precipitation from absolute alcohol by ether. The yield is about 50 per cent. The hydrazine is also conveniently removed by shaking with benzaldehyde in an acid solution, whereby benzalazine is precipitated; the excess of benzaldehyde may be removed by ether. The hydrochloride is finally distilled with caustic potash.

Pyrazoline is a colourless liquid of characteristic, amine-like odour, recalling that of cacao. It boils at  $144^{\circ}$ , and is volatile with steam and with ether vapour. It mixes in all proportions with water and alcohol, but is somewhat less soluble in ether. It forms a cloud with hydrogen chloride, and becomes yellow in the air, at the same time evolving gas, but no pyrazole is formed. It gives a white silver salt; it does not reduce Fehling's solution.

The *hydrochloride*,  $C_3H_5N_2 \cdot HCl$ , crystallises in large, colourless prisms, melts at  $130^{\circ}$ , and dissolves easily in water but sparingly in cold alcohol, and hardly at all in ether. Its solutions, even when very

dilute, colour woody-fibre intensely yellow. The *sulphate*, *platinochloride*, and *picrate* (m. p.  $130^{\circ}$ ) are described.

Pyrazoline shows great resistance to the action of mineral acids, a fact which favours the view that it is a closed chain compound, and forbids the assumption that it is identical with acetaldehydehydrazine. When boiled with concentrated aqueous alkalis, about 10 per cent. of its nitrogen is evolved as ammonia. Most oxidising agents oxidise pyrazoline drastically, causing an evolution of nitrogen, but by the action of bromine on the base or its hydrochloride, suspended in chloroform, pyrazole is produced; on the other hand, bromopyrazole is the product of the action of bromine on an aqueous solution of the hydrochloride. The connection between pyrazoline and pyrazole is thus established.

Benzaldehyde combines energetically with pyrazoline, water being eliminated. *Azobenzene*pyrazoline,  $\text{PhN:N}\cdot\text{C}_3\text{N}_2\text{H}_5$ , formed by the interaction of diazobenzene chloride and pyrazoline hydrochloride, crystallises in large, flat, brick-red prisms, and melts at  $80^{\circ}$ .

3-Methyl-5-dimethylpyrazoline,  $\text{C}_3\text{Me}_3\text{N}_2\text{H}_3$ , is obtained when mesityl oxide and hydrazine hydrate, in molecular proportion, are mixed, the product extracted with ether, and the ethereal solution distilled under diminished pressure. It is a colourless oil of basic properties and characteristic odour, and is decomposed by air; it is freely soluble in water, alcohol, and ether; with silver nitrate, its solutions yield a white precipitate which dissolves on warming. The *hydrochloride*,  $\text{C}_6\text{H}_{12}\text{N}_2\cdot\text{HCl}$ , crystallises in colourless prisms, and melts and decomposes at  $170^{\circ}$ . The *picrate* (m. p.  $138^{\circ}$ ), the *mercuric chloride compound*,  $\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{HgCl}_2$ , the *platinochloride* (m. p.  $186^{\circ}$ ), and the *methiodide* (m. p.  $154^{\circ}$ ), are also described.

1: 3-Benzoylmethyl-5 dimethylpyrazoline,  $\text{C}_6\text{N}_2\text{H}_{11}\text{Bz}$ , from benzoic chloride and the pyrazoline, crystallises in colourless, felted needles, and melts at  $236^{\circ}$ .

A compound,  $\text{C}_{21}\text{H}_{31}\text{N}_6\text{O}_{12}$ , forming colourless crystals, melting at  $223^{\circ}$ , and freely soluble in water, was obtained as a bye-product in the preparation of 1-phenylpyrazoline.

*Benzylidene*-1-phenylpyrazoline,  $\text{CHPh}\cdot\text{C}_3\text{N}_2\text{H}_3\text{Ph}$ , the condensation product of benzaldehyde with 1-phenylpyrazoline, is a white powder, and melts at  $235^{\circ}$ . A second modification was obtained in the form of an ochre-yellow powder of ill-defined melting point.

*Isonitroso*-1-phenylpyrazoline,  $\text{C}_3\text{N}_2\text{H}_3\text{Ph}\cdot\text{NOH}$ , crystallises in small, brick-red needles, and melts at  $148^{\circ}$ . *Benzeneazo*-1-phenylpyrazoline,  $\text{C}_3\text{N}_2\text{H}_4\text{Ph}\cdot\text{N}_2\text{Ph}$ , crystallises in brilliant, purple-red needles, melting at  $156^{\circ}$ ; its *hydrochloride* is described.

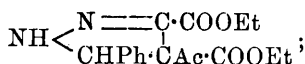
When hydrogen chloride is passed into an ethereal solution of 1-phenylpyrazoline, *bisphenylpyrazoline hydrochloride*,  $\text{C}_{18}\text{H}_{20}\text{N}_4\cdot\text{HCl}$  (?), separates as a greenish oil, which crystallises in slender, colourless needles. It rapidly loses hydrogen chloride, even in air; its acid solutions in alcohol and benzene are dark green by reflected light, but purple-red by transmitted light; it melts at  $175^{\circ}$ . The corresponding *base* crystallises in yellow needles, melts at  $221^{\circ}$ , and dissolves freely in hot benzene, but only sparingly in ether, and not in water. The ethereal solution has a blue fluorescence. The base

dissolves in glacial acetic acid forming a cherry-red solution, whilst with strong sulphuric acid it yields a cherry-red or blue solution, and with strong nitric acid an indigo-blue solution.

A compound of the formula  $C_9H_{17}N_2I$  is obtained from allylic iodide and hydrazine hydrate; it forms colourless crystals, and melts at  $102^\circ$ .

A. G. B.

**Action of Ethylic Diazoacetate on Unsaturated Ethylic Salts.** By EDUARD BUCHNER and AUGUST PAPENDIECK (*Ber.*, 1895, **28**, 221—224).—Ethylic diazoacetate and benzyldieneacetoacetate, when boiled together for three or four days at  $50$ — $75^\circ$ , condense to form ethylic phenylacetylpyrazolinedicarboxylate, probably



this crystallises in colourless needles and melts at  $76^\circ$ ; its phenylhydrazone crystallises from alcohol in needles melting at  $135$ — $136^\circ$ , from ether in plates melting at  $110$ — $111^\circ$ . On hydrolysis of the ethylic salt, the free acid with  $2H_2O$  is obtained; this forms a diphenylhydrazide and a calcium salt with  $5H_2O$ ; its silver salt, when heated in a current of carbonic anhydride, yields 5-phenylpyrazole (*Abstr.*, 1893, i, 282; this vol., i, 192). When the ethylic salt is distilled under 25 mm. pressure, an oil passes over at  $230$ — $242^\circ$ ; this solidifies to colourless plates melting at  $101^\circ$ ; it does not contain nitrogen.

C. F. B.

**Phenometadiazine Derivatives.** By AUGUST BISCHLER and MARTIN LANG (*Ber.*, 1895, **28**, 279—293; compare *Abstr.*, 1893, i, 609).—Pheno- $\beta$ -methylmetadiazine has been previously described (*Abstr.*, 1891, 745). It is not affected by dilute permanganate, but chromic acid in acetic acid solution converts it into pheno- $\beta$ -methylhydroxymetadiazine,  $C_6H_4 < \begin{array}{c} N = \overline{C}Me \\ C(OH):N \end{array}$ , which crystallises in white, silky needles, and melts at  $231.5$ — $232^\circ$ . It appears to be identical with the substance described by Weddige (*Abstr.*, 1887, 1043) as anhydroacetyl-orthamidobenzamide. The platinochloride decomposes above  $300^\circ$ , and the dichromate deflagrates at  $175$ — $176^\circ$ . Propionic anhydride converts orthamidobenzaldehyde into an oil which, on treatment with alcoholic ammonia, yields pheno- $\beta$ -ethylmetadiazine; this is a yellow, oily liquid, which has a sp. gr. of 1.0899 at  $20^\circ$ , and boils at  $247$ — $249^\circ$  (722 mm.). The hydrochloride,  $C_{10}H_{10}N_2 \cdot HCl + H_2O$ , is obtained by passing hydrogen chloride into an ethereal solution of the metadiazine. Pheno- $\beta$ -ethyl- $\alpha$ -hydroxymetadiazine may be sublimed in snow-white, woolly needles, melting at  $227$ — $228^\circ$ . Pheno- $\beta$ -normal-propylmetadiazine boils at  $257$ — $259^\circ$ , and also forms a hydrochloride and a platinochloride. Its hydroxy-compound crystallises in white, bulky needles, which melt at  $205^\circ$ . The platinochloride crystallises well. Pheno- $\beta$ -isopropylmetadiazine boils at  $253$ — $255^\circ$ , whilst the corresponding hydroxy-derivative crystallises in concentric groups of white needles, melting at  $195$ — $196^\circ$ .

Benzylamidobenzaldehyde,  $NHBz \cdot C_6H_4 \cdot CHO$ , forms stellate groups



of yellowish-white, slender needles, melting at 73—74°. *Pheno-β-phenylmetadiazine* has been previously described by Gabriel and Jansen (Abstr., 1890, 1442). The *hydrochloride* crystallises in needles, and is decomposed by warm water. The *platinochloride* and *picrate* are crystalline. *Pheno-β-phenylhydroxymetadiazine* forms lustrous, white needles, and melts at 235—236°. *Pheno-β-benzylmetadiazine* is an odourless; yellow, crystalline mass, which melts at 59—60°, but could not be obtained quite pure. The *hydroxy-compound* forms slender, matted needles, melting at 177°.

Formylamidobenzaldehyde could not be obtained either directly or indirectly. In order to prepare phenometadiazine itself, *ethoxalyl-orthamidobenzaldehyde*,  $\text{COOEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ , was prepared by the action of ethoxalyl chloride on the aldehyde. This crystallises in long, silky needles, melting at 196°, and on hydrolysis yields the corresponding *oxamic acid*, which crystallises in stellate groups of needles, and melts and decomposes at about 163—164°. As the formyl-compound could not be obtained from it, the acid was treated directly with alcoholic ammonia; in this way, a small amount of a yellow oil was obtained, which had the characteristic smell of the phenometadiazines, resembling that of mice, and had the composition of phenometadiazine. The amount obtained was too small for any further experiments.

When crude phenylacetylorthamidobenzaldehyde is treated with alcoholic potash, it yields a substance which crystallises in white needles and melts at 234—235°. This compound, which is probably *phenylhydroxyquinoline*, is being further investigated. A. H.

**Semicarbazide.** By JOHANNES THIELE and OTTO STANGE (*Annalen*, 1894, 283, 1—46; compare Abstr., 1891, 452, and 1894. i, 165).—*Orthonitrobenzylidenesemicarbazide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is obtained by adding orthonitrobenzaldehyde dissolved in alcohol to an aqueous solution of semicarbazide hydrochloride. It crystallises in lemon-yellow needles, which melt and decompose at 256°; the solution in hot soda is red. *Metanitrobenzylidenesemicarbazide* forms pale yellow needles, which melt at 246°, and dissolve in hot soda with development of a yellowish-brown coloration. *Paranitrobenzylidenesemicarbazide* separates from hot alcohol in yellowish-white crystals, melting at 221°; it crystallises from water in lemon-yellow needles containing 2H<sub>2</sub>O. The *sodium salt* is brownish-red.

1 : 2-Diphenylhydroxytriazine,  $\text{N} \begin{smallmatrix} \text{C(OH):N} \\ \text{CPh} \cdot \text{CPh} \end{smallmatrix} \text{N}$ , is obtained by boiling a solution of semicarbazide hydrochloride, which has been neutralised with magnesium carbonate, with an alcoholic solution of benzile (1 mol.) for 15 hours; it crystallises in pale yellow needles, and melts at 218°. The *ethyl ether* forms colourless needles, melting at 105°.

*Ethyl acetoacetate-semicarbazide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{COOEt}$ , is prepared by agitating the solution of semicarbazide hydrochloride with ethyl acetoacetate in presence of sodium acetate; it melts at 129°. When warmed with ammoniacal silver solution, the substance is oxidised, and evolution of gas takes place; potassium permanga-

nate is decolorised on heating. Hydrogen cyanide does not give rise to an additive compound. When heated at  $120^{\circ}$ , ethylic acetoacetate-semicarbazide is converted into 3-methylpyrazolone, which is also formed on boiling the aqueous solution.

3-Methylpyrazolone-1-carbonamide,  $\begin{array}{c} \text{N} \equiv \equiv \equiv \text{CMe} \\ | \\ \text{N}(\text{CONH}_2) \cdot \text{CO} \end{array} > \text{CH}_2$ , is produced when the foregoing compound remains in contact with ammonia for two days; the residue obtained on evaporating the liquid in a vacuum, is dissolved in cold methylic alcohol, and precipitated with ether. The substance melts at  $192^{\circ}$ , and is converted into methylpyrazolone when the aqueous solution is warmed. Ferric chloride develops a blue coloration, which becomes brown when heated.

Ethylic 3-methylpyrazolone-1-carbonyl- $\beta$ -amidocrotonate,



is obtained by agitating semicarbazide hydrochloride with excess of ethylic acetoacetate in presence of soda; it forms small prisms, which melt and decompose at  $176^{\circ}$ . Ferric chloride produces an intense blue coloration. The sodium salt is colourless. When distilled in a current of steam, the substance is decomposed into ethylic acetoacetate, ammonia, carbonic anhydride, and methylpyrazolone.

Carbonamidohydrazoisobutyronitrile,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CN}$ , is obtained by the action of hydrogen cyanide on acetone-semicarbazide, and crystallises in prisms, which melt at  $144^{\circ}$ . It has powerful reducing properties, and is decomposed into hydrogen cyanide and acetone-semicarbazide when the aqueous solution is heated on the water bath.

Carbonamidoazoisobutyronitrile,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} : \text{N} \cdot \text{CMe}_2 \cdot \text{CN}$ , is obtained by oxidising the hydrazo-compound with potassium permanganate in presence of sulphuric acid; it forms lemon-yellow plates, which melt at  $78^{\circ}$ . It is decomposed by cold, dilute alkalis, with liberation of nitrogen, carbonic anhydride, ammonia, and isopropyl cyanide.

Carbonamidohydrazoisobutyramide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CONH}_2$ , is formed by the action of fuming hydrochloric acid on the nitrile; it melts and decomposes at  $205-206^{\circ}$ . When oxidised with potassium permanganate, it yields carbonamidoazoisobutyramide, which separates from hot water in deep yellow crystals, and melts and decomposes at  $151^{\circ}$ .

Carbaminazoimide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_3$ , is obtained by adding sodium nitrite (1 mol.) to the aqueous solution of semicarbazide hydrochloride; it crystallises in large prisms, which melt at  $92-93^{\circ}$ . The aqueous solution is acid, and yields azoimide when boiled. Mercuric chloride produces a white precipitate. The dry solid is volatile, and explodes when heated. One half the total quantity of nitrogen is liberated by a cold solution of stannous chloride in hydrochloric acid. The colourless, highly explosive, silver salt is insoluble in water; it dissolves in ammonia and in dilute nitric acid, whilst concentrated acid decomposes it into silver azoimide, carbonic anhydride, and

ammonia. Carbaminazoimide is also formed by the action of nitrous acid on hydrazodicarbonamide.

*Hydrazodicarbonimide (urazole)*,  $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{NH}$ , is obtained by heating hydrazocarbonamide at  $200^\circ$  for five hours; it melts at  $244^\circ$ . The aqueous solution has powerful reducing properties, and yields a white precipitate with mercuric chloride; cupric acetate produces a green precipitate. Oxidising agents develop a red coloration, due to the formation of azodicarbonimide, which, however, has not been isolated, owing to its extreme volatility and unstable character. The *silver* salt is colourless, and is not decomposed by light; the *sodium* salt separates from water in small plates, which contain  $2\text{H}_2\text{O}$ . The *phenyl* derivative, *hydrazodicarbonanil*, is obtained by heating a mixture of hydrazodicarbonamide and aniline hydrochloride (1 mol.) at  $220^\circ$  for four hours, diphenylcarbamide being formed at the same time. It crystallises from water in prisms, and melts at  $203^\circ$ . The *silver* salt is pale yellow. Oxidising agents convert it into the *azo*-derivative,  $\begin{array}{c} \text{N}\cdot\text{CO} \\ || \\ \text{N}\cdot\text{CO} \end{array} > \text{NPh}$ , a dark red solid, having a pungent odour.

M. O. F.

***r*-Coniïne.** By ALBERT LADENBURG (*Ber.*, 1895, **28**, 163—165).—When 4 grams of *l*-coniïne are mixed with 2 grams of *d*-coniïne at the ordinary temperature, no change of specific gravity occurs, but there is a fall of temperature. This last must be due to the formation of an endothermic compound, and *r*-coniïne is thus a compound, and not a mere mixture, of the two optically active varieties, in spite of the fact that it has the same specific gravity as these. It is consequently not necessary, as E. Fischer thinks it to be, that a racemic compound should have physical properties different from those of its active components.

*d*- and *r*-coniïne have respectively 1.4548 and 1.4581 as their indices of refraction for the D line at  $15^\circ$ , and they dissolve to the extent of 1.80 and 1.93 parts in 100 of water.

C. F. B.

**Conium Alkaloids.** By RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 302—305; compare *Abstr.*, 1894, i, 627).—The author has detected coniceïne in a specimen of coniïne, prepared from *Conium maculatum*. This is identical with the  $\gamma$ -coniceïne described by Hofmann (*Abstr.*, 1885, 562). The *hydrochloride* melts at  $143^\circ$ , the *hydrobromide* at  $139^\circ$ , and the *hydriodide* at  $102^\circ$ . The *stannochloride* crystallises in plates, melting at about  $215^\circ$ ; the *picrate* melts at  $62^\circ$ , and the *aurochloride* at  $69$ — $70^\circ$ . Coniceïne is about 17 times as poisonous as coniïne, and it is probable that the uncertain effect of coniïne when administered may be due to an unsuspected presence of coniceïne.

Coniceïne is optically inactive, and is not resolved into active components by fractional crystallisation with dextrotartaric acid. It follows from this that the ethylene bond must be between the asymmetric carbon atom of coniïne and a neighbouring atom, so that its constitutional formula will be  $\text{NH} < \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CPr}\cdot\text{CH} \end{array} > \text{CH}_2$ .

A. H.

**Cinchoténine.** By ZDENKO H. SKRAUP (*Ber.*, 1895, **28**, 12—16).—A preliminary notice; the full paper is to appear in the *Monatshefte*. Quinine, quinidine, cinchonine, and cinchonidine are known to yield "tenines" and formic acid when cautiously oxidised with permanganate; cinchonine,  $C_{19}H_{22}N_2O$ , for example, yields cinchoténine,  $C_{18}H_{20}N_2O_3$ . It is also known that they are di-tertiary bases, and that they contain a hydroxyl group. This is now shown to be true of the "tenines" also, in particular of cinchoténine, the ethylic salt of which (see below) forms a compound with two molecules of ethylic iodide; this is not decomposed by alkali carbonates. It yields a benzoyl derivative. Further, the "tenines" contain a carboxyl group, for they, as well as their benzoyl derivatives, form metallic salts; they also yield ethylic salts, and acid chlorides. They do not form additive compounds with hydrogen iodide, whereas the alkaloids from which they are derived, do so; it is thus probable that these alkaloids contain an unsaturated (vinyl) group,  $\cdot CH:CH_2$ , as a side chain, and that this group is converted into carboxyl and formic acid when the alkaloids are oxidised to "tenines." Moreover, the bases that occur in the commercial alkaloids, and contain in the molecule 2 atoms of hydrogen more than these (cinchotine, &c.), probably have an ethyl group in place of this vinyl group. Finally, it is pointed out that the relation of cincholeupone,  $C_9H_{17}NO_2$  (formed by oxidation of cinchotine), meroquinine,  $C_9H_{15}NO_2$  (by oxidation of cinchonine), and cincholeuponic acid,  $C_8H_{13}NO_4$ , is that of dihydroalkaloid to alkaloid to "tenine;" for example, of cinchotine : cinchonine : cinchoténine. C. F. B.

**History of Aconitine.** By MARTIN FREUND (*Ber.*, 1895, **28**, 192—195).—Controversial note in reply to Dunstan's claim to priority (*Abstr.*, 1894, i, 308).

**Cytisine and Ulexine.** By PIETER C. PLUGGE (*Arch. Pharm.*, 1894, **232**, 557—558) and by ALFRED PARTHEIL (*ibid.*, 558—559; compare Partheil, *Abstr.*, 1893, i, 119, and 1894, i, 558).—A question of priority.

**Pseudopelletierine.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1894, [3], **11**, 422—423).—A protest against the substitution, by Ciamician and Silber (*Abstr.*, 1894, i, 154), of the name granatone for that of pseudopelletierine. JN. W.

**Chondroitin-sulphuric acid.** By CARL T. MÖRNER (*Zeit. physiol. Chem.*, 1895, **20**, 357—364).—This substance, originally named chondroitie acid, is an ethereal hydrogen sulphate, and has been found in certain forms of cartilage. The present research shows that all kinds of cartilage, from 20 different situations in the body, and also cartilaginous tumours or enchondromata yield it. It is, moreover, a substance characteristic of cartilage, and is not yielded by any other tissue of the body, 14 of which were investigated. W. D. H.

**Coagulation of Proteïds by Mechanical Means.** By W. RAMSDEN (*Archiv. für Anat. u. Physiol. ; physiol. Abth.*, 1894, 517—

534).—By mechanical means, such as shaking with sand, or even pouring from one test-tube to another, a solution of egg-white deposits insoluble proteïd, reminding one of fibrin filaments, which also it resembles in its difficulty of solubility. By prolonged shaking, 96 per cent. of the proteïd present was separated. Other proteïds behave similarly, but, as a rule, in a less degree, namely, egg globulin, vitellin, the proteïds of blood-plasma, myosinogen, potato proteïd, plant vitellin, alkali albumin, and some specimens of caseinogen.

W. D. H.

**Crystallisation of Serum Albumin.** By AUGUST GÜRBER (*Sitzungsber. Würzburger Phys. med. Ges.*, 1894).—Crystals of serum-albumin may be obtained in the course of some weeks from the serum of horse's blood by Hofmeister's method. A new method, not yet divulged, has enabled the author to obtain them more rapidly; the crystals indicate that there are three albumins in the serum. They could not be obtained from ox serum.

W. D. H.

**The Combination of Sulphur in Albumin.** By EUGEN BAUMANN (*Virchow's Archiv*, 1894, 138, 560—562).—Answer to the foregoing. By ERNST SALKOWSKI (*ibid.*, 562—564). Polemical.

**Sulphur in various Keratin Substances.** By P. MOHR (*Zeit. physiol. Chem.*, 1895, 20, 403—406).—Different authors give different percentages of sulphur in different keratins. In the present research, keratin was prepared from various sources, and, as the following table shows, the variations in the percentage of sulphur are considerable.

Source of keratin.	Sulphur per cent.	Source of keratin.	Sulphur per cent.
Woman's hair—dark blonde ..	4·95	Sheep's wool.....	3·68
Girl's hair—dark brown.....	5·34	Goose feathers.....	2·59—3·16
Boy's hair—red blonde.....	4·98	Pig's hoof .....	2·69
Boy's hair—red.....	5·32	Calf's hoof .....	3·57
Rabbit's hair.....	4·01	Ox hoof, white .....	3·49
Calf's hair.....	4·35	Ox hoof, black .....	3·45
Horsehair .....	3·56		
Pig's hair.....	3·59		

W. D. H.

**Amyloid.** By ARMIN TSCHERMAK (*Zeit. physiol. Chem.*, 1895, 20, 343—356).—The substance called amyloid by Virchow, which occurs in a certain form of pathological degeneration, has been shown by Kekule, Kühne, and others to be proteïd in nature.

The present research confirms this, and, moreover, shows that the material in question dissolves easily in alkalis, and less easily in organic and mineral acids, and on peptic and tryptic digestion, and on heating it in a sealed tube in water. The result of the solution is,

first, unchanged amyloid, then albuminate, and, on more prolonged digestion, primary and secondary albumoses and peptone. These products of digestion give the same colour reactions as the original material, sometimes even more intensely.

Amyloid is regarded, like hyalin, as a modified coagulation product of the circulating proteid, probably serum albumin, not fibrin.

W. D. H.

**Methæmoglobin.** By J. A. MENZIES (*J. Physiol.*, 1895, **17**, 402—414).—Oxyhæmoglobin becomes converted into methæmoglobin as the result of exposure to the air, either in solution or in the dried condition; and also as the result of the action of many reagents, of which the following were investigated in the present research: glycerol, potassium chlorate, permanganate and ferricyanide, iodine, amylic nitrite, potassium nitrite, sodium fluoride, and certain acids.

When it is produced by decomposition, the solution becomes acid, and if decomposition proceeds further, whereby the reaction changes to alkaline, a reconversion of hæmoglobin takes place. If produced by the action of reagents, the further action of the same reagents gives rise to hæmatin, which is precipitated, unless held in solution by acids. In the case of potassium ferricyanide, the hæmatin passes into the condition of cyanhæmatin.

Methæmoglobin cannot be distinguished from hæmatin by its spectrum alone, but only by the change produced by a reducing agent; it yields hæmoglobin on reduction, whilst hæmatin yields hæmochromogen; but in the case of potassium chlorate or ferricyanide or of iodine, the hæmochromogen is after a time gradually transformed into hæmoglobin. The action of the nitrite is considered to be due to the liberation of nitrous acid, and it is suggested that the liberation of acid substances from the other reagents employed is the cause of their action.

In the spectrum of methæmoglobin, the only constant feature is the band in the red, but even this varies in position; bands 2 and 3 become paler till they disappear, as the formation of methæmoglobin becomes completed. Band 4 becomes swamped in the general absorption of the violet end as the formation of hæmatin occurs. Methæmoglobin is regarded as an intermediate product between oxyhæmoglobin and hæmatin.

W. D. H.

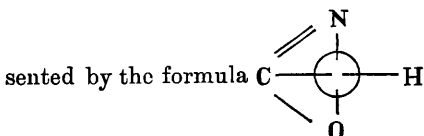
**Action of Acids on Hæmoglobin.** By J. A. MENZIES (*J. Physiol.*, 1895, **17**, 415—422).—Acetic, oxalic, phosphoric, hydrochloric, nitric, and sulphuric acids act on hæmoglobin, converting it first into methæmoglobin, then into hæmatin. The position of the typical absorption band in the red varies with the different acids. By using dilute mineral acid of a certain strength, oxyhæmoglobin can be resolved into a proteid, which remains in solution, and hæmatin, which is precipitated. The latter, when dissolved in dilute acid or alkali, yields hæmochromogen, which, on being mixed with some of the colourless proteid solution, becomes converted into hæmoglobin.

W. D. H.

## Organic Chemistry.

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**Tautomerism.** By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], 51, 338—343).—The author suggests that in tautomeric substances, which yield isomeric series of derivatives, but do not themselves exist in more than one form, one of the atoms (usually a hydrogen atom but sometimes possibly one of sodium, &c.) is not combined with any one particular atom of the molecule, but is held in combination by a common "central" linking with several of the other atoms of the molecule. Cyanic acid, for example, would therefore be repre-



A. H.

**Cyanoethers.** By ALBERT COLSON (*Compt. rend.*, 1894, 119, 1213—1215).—The action of cyanogen chloride at the ordinary temperature on a solution of paraxylylene in moist ether, yields ammonium chloride, a large quantity of carbonic anhydride, and a solid substance which melts at 48° and seems to be a derivative of ether rather than of paraxylylene. The action of cyanogen chloride on washed ether in presence of sunlight yields ammonium chloride, carbonic anhydride, and urethane. The latter is a constant product of the action of cyanogen chloride on ether, as Gautier has observed.

The prolonged action of light on the mixture of cyanogen chloride and ether results in the formation of the compound  $\text{CN}\cdot\text{CHMe}\cdot\text{OEt}$ , which has the composition of ethyllactonitrile. It has an ethereal odour and a burning alcoholic taste, is miscible with water, alcohol, and ether, and boils at 129—130°; sp. gr. = 0.87 at 12°. Longer exposure of the original mixture to light yields a compound of the same composition, which, however, is very slightly soluble in water. It boils at 131° under a pressure of 765 mm., and its molecular weight, like that of the soluble compound, is 99; sp. gr. = 0.824 at 12°. It has an ethereal odour and a burning taste, and is miscible with alcohol and ether.

The soluble and insoluble compounds seem to be physical isomerides; they are both very stable, and, when fused with potash, yield ammonia without any formation of a cyanide. From their mode of formation, it would seem that they are related to lactic acid and not to hydracrylic acid.

C. H. B.

**A New Class of Nitriles.** By ALBERT COLSON (*Compt. rend.*, 1895, 120, 101—104).—The author has previously described (preceding abstract) two isomeric cyanoethers of the type  $\text{OR}\cdot\text{CHMe}\cdot\text{CN}$ , which are very stable, and differ from the lactic nitrile  $\text{OH}\cdot\text{CHMe}\cdot\text{CN}$  and its homologues discovered by Gautier and Sampson, in that when fused with potassium hydroxide they lose their nitrogen as ammonia.

The author gives the name *cyanal* to this so-called lactic nitrile and its homologues.

With acetic chloride, cyanal yields the acetate  $\text{AcO}\cdot\text{CHMe}\cdot\text{CN}$ , which boils at  $169^\circ$  (uncorr.) under a pressure of 760 mm.; sp. gr. = 1.052 at  $0^\circ$ , and 1.032 at  $14^\circ$ ; vapour density normal. It dissolves in 25 times its weight of water, and the solution yields no precipitate with silver nitrate, even after a long time; it is also soluble in ether, alcohol, acetic acid, &c. Cyanal acetate has none of the characteristic properties of nitriles or secondary alcohols. It hydrolyses very slowly even at  $140^\circ$ , but eventually yields aldehyde, acetic acid, and hydrocyanic acid in equal molecular proportions. If cyanal acetate is added to an ammoniacal solution of silver nitrate mixed with some potassium hydroxide, there is immediate formation of a silver mirror. With dry hydrogen chloride, it yields a crystalline compound which will be described later.

*Cyanal propionate*,  $\text{C}_3\text{H}_5\text{O}_2\cdot\text{CHMe}\cdot\text{CN}$ , obtained in a similar way, has similar properties. It boils at  $181\text{--}182^\circ$  under a pressure of 760 mm.; sp. gr. = 1.022 at  $0^\circ$ , and 1.004 at  $18^\circ$ . It has a sweet taste, and dissolves in 30 times its weight of water.

*Propylcyanal acetate*,  $\text{AcO}\cdot\text{CHEt}\cdot\text{CN}$ , boils at  $183^\circ$  under a pressure of 762 mm.; sp. gr. = 1.019 at  $0^\circ$ , and 1.006 at  $12.5^\circ$ . It is only very slightly soluble in water, and splits up into its proximate constituents under the influence of alkalis.

C. H. B.

**Brown-coal Tar.** By FRIEDRICH HEUSLER (*Ber.*, 1895, 28, 488—498; compare *Abstr.*, 1892, 1075).—The fraction of brown-coal tar boiling below  $180^\circ$  contains:—1. Paraffins, in quantity increasing with rise of boiling point. 2. Naphthenes, in small amount. 3. Aromatic hydrocarbons, in quantity decreasing with rise of boiling point. 4. Hydrocarbons of the ethylene series (hexylene, heptylene). 5. Thiophens (thiotolen, thioxen). 6. Ketones (methyl ethyl ketone); and 7. Nitriles, in very small amount.

A sample of coal-tar oil was also proved to contain acetone.

C. F. B.

**Formation of Normal Alkyllic Sulphates when Tar Oils are Washed with Sulphuric acid. A New Method of Separating Alkyllic Sulphates and Sulphonates.** By FRIEDRICH HEUSLER (*Ber.*, 1895, 28, 498—501).—The oil obtained when brown-coal tar oil, boiling at  $150\text{--}160^\circ$ , is washed with strong sulphuric acid is proved to contain decylic sulphate (11.3 grams in 100 c.c.), for, when mixed with aniline and allowed to remain, it yields aniline decylic sulphate,  $\text{C}_{10}\text{H}_{21}\text{O}\cdot\text{SO}_2\cdot\text{ONH}_3\text{Ph}$ , together with decylene.

Aniline alkyllic sulphates are decomposed by boiling with aniline into aniline sulphate and alkylene; aniline alkylsulphonates are not so decomposed. If, therefore, a mixture of sulphate and sulphonate is boiled with aniline and then distilled with steam, aniline and the alkylene from the sulphate pass over, whilst the sulphonate remains behind.

C. F. B.

**Salts of the Acid  $\text{H}_2\text{S}_2\text{O}_3$  (Thiosulphurous acid?).** By FELIX LENGFELD (*Ber.*, 1895, 28, 449—451).—The *methylic* salt  $\text{S}_2(\text{OMe})_2$ ,



is obtained by adding dry sodium ethoxide to a cold solution of sulphur monochloride in light petroleum. It is a pale yellow oil which boils at 41—42° under a pressure of 23 mm., and has an excessively disagreeable, pungent odour. The *ethylic* salt is colourless; it boils at 71—72° under a pressure of 28 mm. M. O. F.

**Calcium Ethoxide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1894, 119, 1266—1268).—When calcium carbide,  $\text{CaC}_2$ , is heated with absolute alcohol at 180°, gas is liberated which is a mixture of acetylene with two other hydrocarbons, one of which is probably methane and the other an olefine containing a larger number of carbon atoms, the composition of the gaseous mixture corresponding with the formula  $\text{C}_4\text{H}_6$ , and the reaction being  $\text{CaC}_2 + 2\text{C}_2\text{H}_5\text{O} = \text{Ca}(\text{OEt})\text{OH} + \text{C}_4\text{H}_6$ . When the solid product is dried in the air and then for a short time over sulphuric acid, it has the composition  $3\text{CaO} \cdot 4\text{EtOH}$ , and is not calcium ethoxide, but an additive compound of calcium oxide and alcohol, analogous to that obtained by the action of barium oxide on methyl alcohol. Very prolonged drying over sulphuric acid results in loss of alcohol and formation of the compound  $\text{Ca}(\text{OEt})\text{OH}$ . Colourless crystals form in the sealed tubes before they are opened, but change to a white, amorphous powder on drying. C. H. B.

**Ether.** By LASSAR-COHN (*Annalen*, 1895, 284, 226—232).—In estimating lactic acid by agitating the ethereal extract with water and estimating the aldehyde formed when the solution is oxidised with manganese dioxide and sulphuric acid (Boas's method), it is obviously of the first importance to obtain ether uncontaminated with alcohol. The method of purification adopted by the author is as follows. 1500 c.c. of ether is heated with 25 grams of sulphuric acid, 20 grams of potassium dichromate, and 50 c.c. of water for 24 hours in a reflux apparatus; it is then distilled and mixed with phenylhydrazine, from which it is distilled in 24 hours. A few grams of salicylic acid is then dissolved in the ether, which is again distilled after 24 hours, and the whole process is repeated. On shaking the product with water, and boiling the aqueous extract with sulphuric acid and manganese dioxide for a few minutes, Nessler's reagent produces a slight precipitate, which corresponds with about 0.001 per cent. of aldehyde. M. O. F.

**Action of Chlorine on Secondary Alcohols.** By A. BROCHET (*Compt. rend.*, 1894, 119, 1270—1272).—The action of chlorine on secondary alcohols is much simpler than its action on primary alcohols. The hydrogen of the  $\text{CHOH}$  group is removed, with formation of a ketone, and substitution of chlorine for hydrogen takes place in the attached radicles in a manner determined by the nature of the latter.

Isopropyl alcohol, when strongly cooled and treated with dry chlorine, yields neither acetone nor isopropyl chloride. The product is *unsymmetrical tetrachloracetone*,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{CCl}_3$ , no lower chlorine derivative being obtained at any stage of the action. This boils at

183°; sp. gr. = 1.624 at 15°/4°;  $n_d = 1.497$  at 18°. When treated with very dilute aqueous potash, it yields chloroform and potassium mono- and tri-chloracetates, without any methylene chloride, and hence the symmetrical derivative,  $\text{CO}(\text{CHCl}_2)_2$ , is not present. It would seem that alkalis can act on the unsymmetrical tetrachloracetone in two ways: (1)  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CCl}_3 + \text{KOH} = \text{CH}_2\text{Cl}\cdot\text{COOK} + \text{CHCl}_3$  and (2)  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CCl}_3 + \text{KOH} = \text{CH}_3\text{Cl} + \text{CCl}_3\cdot\text{COOK}$ .

The action of chlorine on isopropyl alcohol is obviously not strictly analogous to the action of bromine, as observed by Friedel and by Etard.

Methylhexylcarbinol rapidly absorbs dry chlorine, but the liquid must be heated towards the close of the action. The product is a pentachloroketone,  $\text{C}_8\text{H}_{11}\text{Cl}_5\text{O}$ , which yields chloroform when treated with alkalis, and probably has the constitution  $\text{C}_5\text{H}_{11}\cdot\text{CCl}_2\cdot\text{CO}\cdot\text{CCl}_3$ . It is a colourless, viscous liquid, which boils at 174° under a pressure of 15 mm., but decomposes when distilled under the ordinary pressure; sp. gr. = 1.401 at 15°/4°;  $n_d = 1.506$  at 21°. It is insoluble in water, but has a burning taste, and an extremely persistent and disagreeable odour (compare Abstr., 1894, i, 484). C. H. B.

**Purification of Alcohols, Sugars, and other Organic Substances.** By EDMÉ J. MAUMENÉ (*Compt. rend.*, 1894, 119, 1014—1016).—Alcohols can be purified by adding a small quantity of an aqueous solution of potassium permanganate and mixing as intimately as possible. If a small quantity of acid is produced, chalk may be added. The same treatment may be applied to both white and red wines, and their flavour is thereby improved, without any loss of bouquet, and without appreciable loss of colour in the case of red wines. A small quantity of manganese oxides, if any, remaining in the liquid, will be quite innocuous.

Permanganate solution may also be used for the purification of sugar, from which it removes all taste or odour of beetroot or sugar cane. It is likewise employed in Algeria to purify the drinking water used by the troops. C. H. B.

**Specific Rotatory Power of Acetylmaltose and of Maltose.** By ALEXANDER HERZFELD (*Ber.*, 1895, 28, 440—443; compare Ling and Baker, *Trans.*, 1895, 212).—The discrepancy which appears between the author's determination of the specific rotatory power of acetylmaltose and the value obtained by the above-mentioned investigators (*loc. cit.*), must be attributed to the character of the solvent employed; the dissimilarity of crystalline form exhibited by the two preparations remains, however, unexplained.

Acetylmaltose in chloroform solution has  $[\alpha]_D = +61.01^\circ$ , in alcohol  $[\alpha]_D = +60.02^\circ$ , whilst if benzene is employed as solvent,  $[\alpha]_D = +76.54^\circ$ .

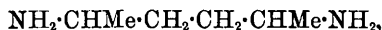
The phenylhydrazone of maltose is decomposed by benzaldehyde; similarly, mannose has been obtained from the phenylhydrazone through the agency of this substance. M. O. F.

**Nitration of Aliphatic Bases.** By EUGEN BAMBERGER and ALFRED KIRPAL (*Ber.*, 1895, **28**, 535—538; compare this vol., i, 273).—By heating the nitrates of the respective bases with acetic anhydride, the following nitro-derivatives were prepared. Nitropiperidine,  $C_5NH_{10} \cdot NO_2$ , mixed with some nitrosopiperidine,



Nitrodimethylamine,  $NMe_2 \cdot NO$ . These substances are identical with those prepared by Franchimont by an indirect method. C. F. B.

**Isomeric 2:5-Diamidohexanes.** By HEINRICH GÜNTHER and JULIUS TAFEL (*Ber.*, 1895, **28**, 379—385).—Diamidohexane,



prepared by reducing the biphenylhydrazone of acetylacetone (*Abstr.*, 1889, 976), can be separated into two isomerides by means of its dibenzoyl derivative, which is found to be a mixture of two substances that can be separated by the difference in their solubilities in alcohol, and then reconverted into diamidohexanes by heating with hydrochloric acid at  $145^\circ$ . The diamidohexanes themselves exhibit a like chemical behaviour, and doubtless stand to one another in the relation of racemic to inactive mesotartaric acid, although it has not as yet been possible to separate either of them into optically active constituents. They boil at nearly the same temperature, and as this is also the case with ethylic racemate and mesotartrate, substances of quite different constitution from the diamidohexanes, the author thinks it may be a general law that "two substances that are only isomeric in the sense of racemic and mesotartaric acids, have approximately the same boiling point." One diamidohexane and its derivatives melt at a higher temperature, and are less soluble than the corresponding isomerides; the former are denoted by  $\phi$ , the latter by  $\chi$ .

$\phi$ -Diamidohexane boils at  $175.5^\circ$  under 753 mm. pressure; the platinochloride decomposes at  $230^\circ$  without melting; the dibenzoyl derivative melts at  $238^\circ$  (uncorr.), and, when melted, or when allowed to remain in strong hydrochloric acid solution, is transformed into a modification insoluble in hydrochloric acid.

$\chi$ -Diamidohexane boils at  $174.5$ — $175^\circ$  under 752 mm. pressure; the platinochloride melts and decomposes at  $211^\circ$ , and the dibenzoyl derivative melts at  $193$ — $198^\circ$ . C. F. B.

**Combination of Hexamethylenetetramine with Silver Salts.** By MARCEL DELÉPINE (*Compt. rend.*, 1894, **119**, 1211—1213).—The compound  $C_6H_{12}N_4 \cdot AgNO_3$  is obtained in tabular crystals by mixing aqueous solutions of its proximate constituents; the compound  $C_6H_{12}N_4 \cdot 4AgCl$  is formed by the action of hydrochloric acid on the preceding compound, or of hexamethylenetetramine hydrochloride on silver nitrate solution, and crystallises from ammonia in prisms. The compound  $5C_6H_{12}N_4 \cdot 3Ag_2CO_3 + 15H_2O$  is obtained by the action of air or carbonic anhydride on an ammoniacal solution of silver oxide and hexamethylenetetramine, and forms acicular crystals. All these compounds are unstable, and yield silver mirrors when their solutions are heated. C. H. B.

**Action of Ammonia on Methylenic Chlorobromide.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1894, [3], 11, 549—556).—Methylenic chlorobromide (1 mol.) reacts with saturated methylic alcoholic ammonia (2 mols.) at the ordinary temperature, quantitatively, but very slowly, yielding *hexamethylenetetramine hydrobromide*,  $C_6H_{12}N_4 \cdot HBr$ , a substance forming hard, brilliant, highly-refractive crystals, and identical with that prepared from hexamethylenetetramine made from formaldehyde. At 60—70°, the action is complete in two hours. The hydrobromide, like the free base, is converted by nitrous acid into dinitrosopentamethylenetetramine,  $C_6H_{10}N_4(NO)_2$ . It is extremely easily hydrolysed by water, and is converted into the free base by lime, but the yield is very poor. It forms a double salt with silver bromide, so that the base cannot be liberated by means of silver oxide. The hexamethylenetetramine dibromide precipitated by bromine from solutions of the base is not amorphous, as stated by Horton (*Abstr.*, 1888, 1051), but, on exposure to air, loses excess of bromine, and then crystallises in characteristic, microscopic, oblique parallelepipeds. JN. W.

**Action of Ammonia on Methylenic Chloride.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1894, [3], 11, 556—557).—Methylenic chloride interacts with saturated methylic alcoholic ammonia scarcely at all at the ordinary temperature, but at 100° the action is complete in eight hours. The hexamethylenetetramine hydrochloride formed was identified by conversion into the dibromide and the nitroso-compound (compare preceding Abstract). JN. W.

**Constitution of Hexamethylenetetramine.** By R. CAMBIER and A. BROCHET (*Compt. rend.*, 1895, 120, 105—107).—The authors ascribe to hexamethylenetetramine the constitution  $N(CH_2 \cdot N \cdot CH_2)_3$ . This formula shows clearly the properties of compound ammonias, explains the easy conversion of the amine into formaldehyde and ammonia in presence of excess of acid, and also explains the action of nitrous acid, which, with excess of the amine, yields carbonic anhydride and dinitrosopentamethylenetetramine, and with excess of the acid yields trinitrosotrimethylenetriamine. The formula indicates the possible formation of additive products of the type  $C_6H_{12}N_4R_6$ , whilst only the terms  $R_2$  and  $R_4$  are known, but there is evidence that the type  $R_4$  is the limit of additive products of this class. According to the formula, hexamethylenetetramine stands in the same relation to ammonia as the methyleneamidoacetonitrile of Jay and Curtius does to hydrocyanic acid.

The formation of methylamine from the tetramine is not due, as Trillat and Fayollat supposed (*Abstr.*, 1894, i, 64) to hydrogenation, but to a secondary action which will be described later.

C. H. B.

**Methanehydrazomethane.** By CARL D. HARRIES and E. KLANT (*Ber.*, 1895, 28, 503—505).—*Methanehydrazomethane*,  $NHMe \cdot NHMe$ , is prepared, like the ethane derivative (*Abstr.*, 1894, i, 568), from lead diformylhydrazine and methylic iodide, the former compound being prepared from normal, not from basic, lead acetate; after purifica-

tion with potash and baryta, the base boils at 50—60°. It is a colourless, highly refractive liquid, fumes strongly in the air, has an unpleasant, amine-like odour, and readily reduces Fehling's solution at the ordinary temperature. The *sulphate* and *hydrochloride* crystallise in deliquescent, colourless plates. The *benzoyl derivative* is insoluble; the *thiosemicarbazide* is crystalline. The *picrate* and *platinochloride* have also been prepared. Compared with ethanehydrazoethane, the methane derivative is more readily prepared, and its compounds crystallise better.

J. B. T.

**Hydrazides of Monobasic and Dibasic Acids of the Fatty Series.** By THEODOR CURTIUS, G. SCHÖFER, and N. SCHWAN (*J. pr. Chem.*, 1895, [2], 51, 180—196; compare this vol., i, 32).—*Formhydrazide*,  $\text{CHO}\cdot\text{NH}\cdot\text{NH}_2$ , prepared from ethylic formate and hydrazine hydrate, crystallises in large, transparent, hygroscopic tablets and in long needles, melts at 54°, and is very soluble in alcohol, ether, chloroform, and benzene; it is decomposed by all dilute acids, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. *Benzylideneformylhydrazine*,  $\text{COH}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , is the product of the condensation of formhydrazide with benzaldehyde; it crystallises in lustrous, white needles, and melts at 134°. *Parahydroxybenzylideneformylhydrazine*, from parahydroxybenzaldehyde and formhydrazide, crystallises in white laminæ, and melts at 243°. *Ethylic formylhydrazoneacetoacetate*,  $\text{CHO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt}$ , from ethylic acetoacetate and formhydrazide, crystallises in white laminæ, and melts at 91°. *Diethylhydrazine*,  $\text{CHO}\cdot\text{NH}\cdot\text{NH}\cdot\text{COH}$ , is obtained when an excess of ethylic formate is heated at 100—130° with hydrazine hydrate in a sealed tube; also by dissolving iodine in an alcoholic solution of formhydrazide until the liquid is permanently yellow; it crystallises in long, lustrous, colourless prisms, melts at 159—160°, and is freely soluble in water, but only sparingly so in alcohol, and insoluble in ether; it reduces ammoniacal silver nitrate, when warmed with it; it does not restore the colour to bleached magenta solution, nor combine with sodium sulphite, but it yields formylphenylhydrazine with phenylhydrazine.

*Acethylhydrazide*,  $\text{CMeO}\cdot\text{NH}\cdot\text{NH}_2$ , crystallises in colourless, hygroscopic needles, melts at 62°, and dissolves in water and in alcohol; the aqueous solution is neutral, and reduces Fehling's solution when warmed. The *benzylidene* compound crystallises in colourless needles, melts at 134°, and is sparingly soluble in water. *Cyanacetylhydrazide* has been described (*Abstr.*, 1894, i, 272). *Cyanacetylacetonehydrazine*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$ , crystallises in needles, and melts at 152°.

*Malonhydrazide*,  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ , is prepared from ethylic malonate and hydrazine hydrate in molecular proportion; it crystallises in needles and laminæ, melts at 152°, and dissolves sparingly in cold water and dilute alcohol, but not in ether; it is very stable towards dilute acids, its *hydrochloride* being precipitated on the addition of strong hydrochloric acid to its aqueous solution. *Benzylidenemalonylhydrazine*,  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$ , crystallises in small, sparingly soluble needles, and melts at 226°. *Parahydroxybenzylidene-*

*malonylhydrazine*,  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , is a white crystalline powder which melts at  $163^\circ$ , and dissolves in absolute alcohol. *Cinnamylidenemalonylhydrazine*,  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh})_2$ , is a white powder which melts at  $217^\circ$ , and dissolves in hot, absolute alcohol.

*Succinhydrazide*,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ , crystallises in white, silvery laminæ, melts at  $167^\circ$ , and dissolves in water; it resembles malonhydrazide in general behaviour. The *hydrochloride* was prepared. When succinhydrazide is heated above its melting point, it loses a little water and hydrazine, and then solidifies to a mass which is insoluble in hot water and alcohol. *Benzylidenesuccinylhydrazine*,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$ , crystallises in nacreous laminæ, and is more soluble in alcohol than is the malonyl-derivative. *Parahydroxybenzylidenesuccinylhydrazine* is a white crystalline powder which melts at  $216^\circ$ , and dissolves easily in absolute alcohol. *Cinnamylidenesuccinylhydrazine*,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh})_2$ , forms a white powder, melts at  $239^\circ$ , and is very sparingly soluble. *Acetophenonesuccinylhydrazine*,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMePh})_2$ , is a white powder, melts at  $238^\circ$ , and is very sparingly soluble in absolute alcohol. When succinhydrazide (1 mol.) is treated with sodium nitrite (2 mols.) and acetic acid, much nitrogen is evolved, and a white precipitate,  $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$ , separates; this is insoluble in most solvents, but soluble in alkalis and in dilute sulphuric acid; it yields a white, silver compound unstable in air.

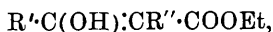
*Oxalhydrazide*,  $\text{C}_2\text{O}_2(\text{NH}\cdot\text{NH}_2)_2$ , obtained from ethylic oxalate and hydrazine hydrate, crystallises in long, thick needles which decompose at  $235^\circ$ ; it reduces Fehling's solution less easily than do succin- and malonhydrazide, than which it is less soluble, but which it otherwise resembles. The *hydrochloride* is described. When oxalhydrazide is treated with sodium nitrite and acetic acid, a white compound of the empirical formula  $\text{C}_2\text{N}_2\text{O}_2\text{H}_2$  is obtained; this appears to be also the product of the action of mercuric oxide on the hydrazide. *Benzylideneoxalhydrazine* crystallises in white laminæ, melts above  $250^\circ$ , and is insoluble in water, and very sparingly soluble in alcohol. *Parahydroxybenzylideneoxalhydrazine* and *cinnamylideneoxalhydrazine* are also sparingly soluble compounds which melt above the boiling point of strong sulphuric acid.

A. G. B.

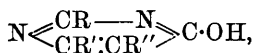
**Thiamines.** By FELIX LENGFELD and JULIUS STIEGLITZ (*Ber.*, 1895, 28, 575—576).—*Tetraethylthiodiamine*,  $\text{S}(\text{NEt}_2)_2$ , is prepared from sulphur dichloride and diethylamine; it is a pale yellow, oily liquid with a pleasing smell, and darkens by prolonged exposure to air. It boils at  $87$ — $87.5^\circ$  under a pressure of 19 mm., and at about  $190^\circ$  under the ordinary pressure, part being decomposed. Concentrated acids decompose it immediately, and sulphur is liberated, whereas potash and water act only slowly. Cryoscopic molecular weight determinations agree with the above formula, which indicates that sulphur dichloride is  $\text{SCl}_2$  and not  $\text{S}_2\text{Cl}_2 + \text{Cl}_2$ . J. B. T.

**Imido-ethers.** By ADOLF PINNER (*Ber.*, 1895, 28, 473—488).—An imido-ether,  $\text{R}\cdot\text{C}(\text{NH})\cdot\text{OR}'$ , is obtained as hydrochloride by pass-

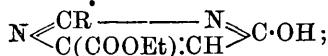
ing hydrogen chloride into a solution of the cyanide,  $R \cdot CN$ , in the alcohol,  $R'OH$ . Ammonia converts it into an amidine,  $R \cdot C(NH) \cdot NH_2$ ; a primary amine,  $NH_2R'$ , and a secondary amine,  $NHR'_2$ , convert it respectively into a symmetrical and an unsymmetrical substituted amidine,  $R \cdot C(NR') \cdot NHR'$  and  $R \cdot C(NH) \cdot NR'_2$ . With diazobenzene, the amidine,  $R \cdot C(NH) \cdot NH_2$ , yields a compound,  $R \cdot C(NH) \cdot NH \cdot N : NPh$ ; with phenylcarbimide, a diureide,  $NHPh \cdot CO \cdot N : CR \cdot NH \cdot CO \cdot NHPh$ , and sometimes also a ureide,  $R \cdot C(NH) \cdot NH \cdot CO \cdot NHPh$ ; with phenylthiocarbimide, a thiocarbamide,  $R \cdot C(NH) \cdot NH \cdot CS \cdot NHPh$ ; with ethylic chloroformate, a urethane,  $R \cdot C(NH) \cdot NH \cdot COOEt$ ; with carbonyl chloride, a carbamide,  $CO[NH \cdot CR(NH)]_2$ , and then a hydroxycyanidine,  $N \begin{smallmatrix} \diagup CR \cdot N \\ \diagdown CR : N \end{smallmatrix} C \cdot OH$ ; with acetic anhydride and sodium acetate, an acetylamido-derivative,  $R \cdot CO \cdot NHAc$ , together with a methylcyanidine,  $N \begin{smallmatrix} \diagup CR \cdot N \\ \diagdown CR : N \end{smallmatrix} CMe$ ; with derivatives



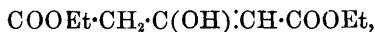
of the type of ethylic acetoacetate, hydroxypyrimidines,



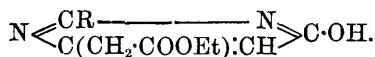
are formed; with ethylic oxalacetate,  $COOEt \cdot C(OH) : CH \cdot COOEt$ , it yields a salt of a hydroxypyrimidinecarboxylic acid,



and with ethylic acetonedicarboxylate,



a salt of a hydroxypyrimidineacetic acid,



The substances enumerated below were prepared by means of these reactions; the numbers given are melting points, the substances often decomposing at the same time. Many of the derivatives of nitrobenzamidine were converted by reduction into the corresponding amidobenzamidine derivatives.

Starting point, hexylic cyanide.—*Heptenylimidoethers*,



the *hydrochlorides* of the *methyl* ( $88^\circ$ ), *ethyl* ( $67^\circ$ ), and *propyl* ( $70^\circ$ ) ethers are very hygroscopic; those of the *butyl* and *amyl* ethers could only be obtained as a mixture of crystals and syrup; they yield alkyl chloride and *œnanthylamide* when heated; the free ethers cannot be obtained from them. *Heptenylamidine hydrochloride*,  $66^\circ$ ; *platinochloride*, yellow,  $157^\circ$ ; *nitrate*,  $131^\circ$ ; *chromate*, yellow,  $149^\circ$ ; *picrate*, yellow,  $152^\circ$ . *Dimethylheptenylamidine*; *symmetrical*, *platinochloride*,  $183^\circ$ ; *unsymmetrical*; *hydrochloride*,  $83-84^\circ$ ; *platinochloride*, yellow,  $178^\circ$ . *Heptenyldiphenyldiureide*,  $170^\circ$  (when boiled with

alcohol, yields heptoylphenylcarbamide,  $C_6H_{13}\cdot CO\cdot NH\cdot CO\cdot NHPh$ ,  $89^\circ$ ). *Hexylmethylhydroxypyrimidine*,  $82^\circ$ ; *hexyldimethylhydroxypyrimidine*,  $102^\circ$ ; *hexylmethylethylhydroxypyrimidine*,  $89^\circ$ ; *hexylphenylhydroxypyrimidine*,  $167^\circ$ . *Hexylhydroxypyrimidinecarboxylic acid*,  $219^\circ$ .

Starting point, ethylic cyanacetate.—*Ethylic imidomalonate hydrochloride*,  $COOEt\cdot CH_2\cdot C(NH)\cdot OEt\cdot HCl$ ,  $102^\circ$  (when heated, yields ethylic chloride and ethylic malonamate,  $COOEt\cdot CH_2\cdot CONH_2$ ,  $50^\circ$ ). *Imidomalonamide* (an amidine,  $NH_2\cdot CO\cdot CH_2\cdot C(NH)\cdot NH_2$ ) hydrochloride, decomposes at  $150^\circ$  without melting; aniline salt of diphenylacetamidinecarboxylic acid,  $COONH_3Ph\cdot CH_2\cdot C(NPh)\cdot NHPh$ ,  $223^\circ$ . *Acetamidomethylhydroxypyrimidine*,  $250^\circ$ ; *acetamidophenylhydroxypyrimidine*,  $243^\circ$ .

*Phenylhydroxypyrimidineacetic acid*, when heated, loses carbonic anhydride, and forms phenylmethylhydroxypyrimidine, melting at  $216^\circ$ ; *ethylic salt*,  $155^\circ$ ; *silver salt*, with  $1H_2O$ , at  $268^\circ$  when anhydrous. 1 : 4-*Tolylhydroxypyrimidineacetic acid*, when heated, yields 1 : 4-tolylmethylhydroxypyrimidine, melting at  $214^\circ$ ; *ethylic salt*,  $164^\circ$ . *Ethylic  $\beta$ -naphthylhydroxypyrimidineacetate*,  $193^\circ$ . *Ethylic furfurylhydroxypyrimidineacetate*,  $164^\circ$ .

Starting point, 1 : 3-nitrobenzonitrile.—*Metanitrobenzamidinediazobenzene*, brownish-yellow,  $160^\circ$ . *Metanitrobenzenyldiphenyldiureide*,  $173^\circ$ ; *nitrobenzimidophenylureide*,  $157^\circ$ . *Metanitrobenzimidophenylthiocarbamide*,  $169$ — $170^\circ$ . *Metanitrobenzamidineurethane*,  $176^\circ$ . *Metadinitrodiphenylhydroxycyanidine*,  $238$ — $240^\circ$ . *Acetylnitrobenzamide*, yellowish,  $198^\circ$ ; *metadinitrodiphenylmethylcyanidine*, yellowish-brown,  $185^\circ$ . *Metanitrophenylmethylhydroxypyrimidine*,  $254^\circ$ ; *metanitrophenyldimethylhydroxypyrimidine*, above  $300^\circ$ ; *metanitrophenylmethylethylhydroxypyrimidine*,  $263^\circ$ ; *metanitrophenylphenylhydroxypyrimidine*,  $271^\circ$ . *Metanitrophenylhydroxypyrimidinecarboxylic acid*,  $260^\circ$ . *Amidobenzamidine hydrochloride* ( $2HCl + H_2O$ ),  $260^\circ$ ; *platinochloride*, decomposes without melting. *Amidobenzamidinediazobenzene*,



*Amidobenzamidine diurethane*,  $COOEt\cdot NH\cdot C_6H_4\cdot C(NH)\cdot NH\cdot COOEt$ ,  $152$ — $153^\circ$ . *Amidophenylmethylhydroxypyrimidine*,  $177^\circ$ ; hydrochloride ( $HCl + 5H_2O$ ),  $265^\circ$  when anhydrous; *platinochloride* ( $H_2PtCl_6 + 2H_2O$ ) loses  $1H_2O$  at  $100^\circ$ , the second at  $130$ — $140^\circ$ . C. F. B.

**Ethylenemethylal.** By LOUIS HENRY (*Compt. rend.*, 1895, 120, 107—110).—According to Trillat and Cambier (*Abstr.*, 1894, i, 487), the product of the action of trioxymethylene on ethylene glycol is the methylene derivative of the latter,  $CH_2(O\cdot CH_2\cdot CH_2\cdot OH)_2$ , and they describe it as a liquid boiling at  $74$ — $75^\circ$ , and only slightly soluble in water. The boiling point of diethylmethylal is about  $85^\circ$ , and since it is improbable that the primary dihydroxyl derivative of this compound would be less volatile, the author has repeated Trillat and Cambier's experiments with trioxymethylene and ethylene glycol. He finds that the product is *ethylenemethylal*,  $CH_2\begin{smallmatrix} O\cdot CH_2 \\ | \\ O\cdot CH_2 \end{smallmatrix}$ , a limpid, mobile liquid with a piquant odour and burning taste, miscible with water in all proportions. It boils at  $78^\circ$  under a pressure of 750 mm. ;



sp. gr. = 1.0828 at 3°; vapour density, 2.50, the calculated value for  $C_3H_6O_2$  being 2.55, and that for  $C_5H_{12}O_4$ , 4.69. Ethylenemethylal has the same relation to methylal as ethylene oxide has to methylic ether, and similar differences are observed between their boiling points. In general reactions it is analogous to the ethyleneacetal described by Wurtz. When subjected to repeated distillation, it seems to split up into methylene and ethylene oxides.

The author has obtained the dichlorinated derivative of dihydroxy-diethylmethylal,  $CH_2(O\cdot CH_2\cdot CH_2Cl)_2$ , by the action of chloromethyl chlorethyl ether,  $CH_2Cl\cdot O\cdot CH_2CH_2Cl$ , on glycol monochlorhydrin, the chlorinated ether being obtained by the action of hydrogen chloride on an aqueous solution of methanal in presence of glycol monochlorhydrin.

C. H. B.

**Dibromosebacic Acids.** By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], 51, 335—338).—The dibromosebacic acid obtained by Weger (Abstr., 1894, i, 359) by the action of phosphorus tribromide and bromine on sebacic acid at a low temperature, is quite a different substance from that prepared by Claus and Steinkauler (Abstr., 1888, 133) by the action of bromine alone at 160—170°, and yields a different hydroxy-acid.

A. H.

**Amidofumarates.** By R. THOMAS-MAMERT (*Bull. Soc. Chim.*, 1894, [3], 11, 480—486).—The amidofumaramide from ethylic chlorofumarate is identical with the final product of the action of ammonia on ethylic oxalacetate, and is hydrolysed by dilute acids yielding the diamide of the latter acid. The intermediate product of the action of alcoholic ammonia on ethylic chlorofumarate at the ordinary temperature is *ethylic chlorofumaramate* (m. p. 101°), and not a maleic acid derivative, as stated by Claus and Voeller (Abstr., 1882, 254). At 100°, the chief product is *ethylic amidofumarate*, a colourless, highly refractive, oily liquid, boiling at 142—143° (20 mm.). This substance is also formed by the action of dry or alcoholic ammonia on ethylic oxalacetate; an intermediate, indefinite, white, curdy product, probably additive, is formed, and is converted by dehydration into the amidofumarate. Ethylic amidofumarate is converted by copper acetate, in presence of alcohol and acetic acid, into *copper ethylic oxalacetate*, which crystallises in transparent, grass-green needles. *Potassium ethylic amidofumarate* crystallises in white plates. Ethylic amidofumarate is converted by aqueous ammonia into a substance forming highly refractive, triclinic crystals, and melting at 102°, possibly ethylic diamidosuccinate.

JN. W.

**Aromatic Acidyltartrates and Anhydrides.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1894, [3], 11, 470—477; compare this vol., i, 174, 210).—The anhydrides are prepared from anhydrous tartaric acid and the acid chloride.

*Dibenzoyltartaric acid*,  $C_2H_5(Obz)_2(COOH)_2 + H_2O$ , melts at 130°. The *anhydride* crystallises in needles, and melts at 174°; its specific rotatory power in acetone solution is  $[\alpha]_D = +142.9^\circ$ . *Diphenylacetyltartaric acid*,  $C_2H_5(O\cdot CO\cdot CH_2Ph)_2(COOH)_2$ , melts at 95—96°. The *anhydride* crystallises in clinorhombic plates, and melts at 117.5°;

its specific rotatory power in acetone solution is  $[\alpha]_D = +60.8^\circ$ . *Diphenylpropionyltartaric anhydride* and *diparatoluoyltartaric anhydride* could not be completely purified; the rotatory power of the former in acetone solution is approximately  $[\alpha]_D = +38.3^\circ$ . *Dicinnamoyltartaric anhydride* crystallises in slender, silky needles, and melts and decomposes slightly at  $147-148^\circ$ ; its specific rotatory power in acetone solution is  $[\alpha]_D = +203.2^\circ$ .

The rotatory powers of the first three homologues become less dextrogyrate as the series is ascended, in accordance with Guye's law. The high rotatory power of the cinnamoyl derivative may be due to the shortening of the phenylpropionic chain, and consequent diminution of its moment, caused by the ethylene linkage.

The alkylic benzoyl- and toluoyl-tartrates were prepared by the action of hydrogen chloride on an alcoholic solution of the anhydride or acid. The other acidyl tartrates described are hydrolysed by hydrochloric acid, and were prepared by the action of the acid chlorides on the alkylic tartrates; they can be distilled unchanged.

*Methylic dibenzoyltartrate* crystallises in clinorhombic prisms, sometimes hemihedral, and melts at  $132^\circ$ ; the specific rotatory power in alcoholic solution is  $[\alpha]_D = -96.6^\circ$ . The *ethylic* salt melts at  $56-58^\circ$ ; the specific rotatory power in alcoholic solution is  $[\alpha]_D = -68.4^\circ$ . The *propylic* and *isobutylic* salts are viscous liquids difficult to purify; the specific rotatory power of the latter in alcoholic solution is  $[\alpha]_D = -42.9^\circ$ .

*Methylic diparatoluoyltartrate* crystallises in acicular, monoclinic prisms, and melts at  $85^\circ$ ; the specific rotatory power in alcoholic solution is  $[\alpha]_D = -89.1^\circ$ .

The diphenylacetyltartrates are highly refractive, viscous liquids, difficult to purify. The *methylic* salt has a sp. gr. = 1.223 at  $17^\circ$ ; the specific rotatory power of the liquid at  $18^\circ$  is  $[\alpha]_D = +14.5^\circ$  that of the alcoholic solution,  $[\alpha]_D = +19.7^\circ$ . The *ethylic* salt has a sp. gr. = 1.174 at  $17^\circ$ ; the specific rotatory power of the liquid is  $[\alpha]_D = +15.3^\circ$ , that of the alcoholic solution,  $[\alpha]_D = +20.2^\circ$ . The *propylic* salt has a sp. gr. = 1.143 at  $18^\circ$ ; the specific rotatory power of the liquid at  $19^\circ$  is  $[\alpha]_D = +20.9^\circ$ , that of the alcoholic solution  $[\alpha]_D = +25.2^\circ$ .

The rotatory powers of the benzoyl and toluyl derivatives thus vary in accordance with Guye's law, with regard to change both of acidyl and of alkyl groups. The diphenylacetyltartrates should, however, be more lævogyrates than the isomeric diparatoluoyl compounds, and not dextrogyrate as is the case.

The specific rotatory power of solutions of the aromatic acidyl tartrates varies considerably with the nature of the solvent. That of *ethylic* diphenylacetyltartrate, for example, varies in solutions of the same concentration from  $+50.1^\circ$  in carbon disulphide to  $+22.1^\circ$  in acetic acid, and  $+14.0^\circ$  in benzene. The value in acetone solution,  $+14.6^\circ$ , is nearest that of the liquid itself,  $+15.3^\circ$ , and does not vary with the concentration. The cryoscopic results obtained with solutions of *propylic* diphenylacetyltartrate in some of the same solvents were also anomalous, as the author has previously observed in other cases (compare this vol., ii, 194).

JN. W.

**Trimethylenepolycarboxylic acids.** By EDUARD BUCHNER (*Annalen*, 1895, **284**, 197—212).—This paper contains a classification of some of the properties of trimethylenepolycarboxylic acids, and some interesting considerations regarding their configuration.

M. O. F.

**trans-1:2-Trimethylenedicarboxylic acid.** By EDUARD BUCHNER and AUGUST PAPENDIECK (*Annalen*, 1895, **284**, 212—219).—The dimethylic salt of *trans*-1:2-trimethylenedicarboxylic acid is obtained by heating methylic pyrazoline-3:5-dicarboxylate (Abstr., 1890, 736); the acid forms crystals which belong to the monosymmetric system,  $a:b:c = 1.8926:1:\rho$ .  $\beta = 59^\circ 00'$ . The *calcium* salt forms small crystals, which contain  $4\frac{1}{2}\text{H}_2\text{O}$ . A hundred parts of water at  $19.5^\circ$  dissolve 19.69 parts of the acid. The *trans*-acid does not form an anhydride; the silver salt, however, yields the anhydride of the *cis*-modification when heated. The heat of combustion of the *trans*-acid is 479.8 Cals., whilst the value obtained by Stohmann and Kleber for the *cis*-modification is 484.1 Cals. (Abstr., 1892, 1041). *Penicillium glaucum* and *Aspergillus niger* have scarcely any action on either of the isomerides; in this point they resemble 1:1-trimethylenedicarboxylic acid, and differ from *cis*-glutaconic acid.

**cis-1:2-Trimethylenedicarboxylic acid** crystallises in large prisms belonging to the monosymmetric system;  $a:b:c = 0.9435:1:0.4950$ .  $\beta = 65^\circ 56'$ . A hundred parts of water at  $20^\circ$  dissolve 112.9 parts of the acid. When heated with sulphuric acid for three hours at  $150^\circ$ , it is converted into the *trans*-modification, which is also formed by the action of fused potash.

M. O. F.

**trans-1:2:3-Trimethylenetricarboxylic acid.** By EDUARD BUCHNER and HUGO WITTER (*Annalen*, 1895, **284**, 219—226).—The trimethylic salt of *trans*-1:2:3-trimethylenetricarboxylic acid is obtained by heating methylic pyrazoline-3:4:5-tricarboxylate (Abstr., 1888, 1274). The acid crystallises from concentrated aqueous solutions in small needles, and melts at  $220^\circ$ . 106.6 parts are dissolved by 100 parts of water at  $9^\circ$ . The trimethylic salt melts at  $59^\circ$  (compare *loc. cit.*); the *calcium* salt contains  $8\text{H}_2\text{O}$ . The *barium* salt contains  $1\text{H}_2\text{O}$ ; the *copper* and *silver* salts are anhydrous. The *amide* of the dimethylic salt forms colourless needles which melt at  $185^\circ$ . The anhydride,  $\text{O} < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_3\text{H}_3\cdot\text{COOH}$ , which melts at  $189^\circ$  (*loc. cit.*), is obtained by the action of boiling acetic chloride on the acid, and also by heating the silver salt.

Methylic *cis*-1:2-*trans*-1:3-trimethylenetetracarboxylate (Abstr., 1885, 1125) melts at  $85^\circ$ . The acid melts at  $196\text{--}198^\circ$  (compare *loc. cit.*), with evolution of gas, being converted into *trans*-1:2:3-trimethylenetricarboxylic acid. Experiments having for their object the preparation of *cis*-1:2:3-*trans*-1-trimethylenetetracarboxylic acid were unsuccessful.

M. O. F.

**Metallic Derivatives of Formylcarbamide, Acetylcarbamide, and Oxaluric acid.** By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], **11**, 573—575).—The acidyl derivatives of carbamide form metallic compounds by replacement of amidic hydrogen.

*Mercuryformylcarbamide*, probably  $\text{CHO}\cdot\text{N}<\overset{\text{CO}}{\underset{\text{Hg}}{\text{C}}}>\text{NH}_2\cdot\text{H}_2\text{O}$ , is a white precipitate, as is the *silver* compound. *Mercuryacetylcarbamide*, probably  $(\text{NHg}\cdot\text{CO}\cdot\text{Nac})_2\text{Hg}$ , is decomposed by light. The greater relative amount of mercury is probably due to the increased acidity caused by introduction of the acetyl group. The *silver* and *cuprous* compounds are white. *Basic calcium oxalurate*, probably  $\text{CO}<\overset{\text{CO}}{\underset{\text{O}\cdot\text{Ca}}{\text{C}}}>\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ , is a white, crystalline precipitate.

JN. W.

**Salts of Carbamide.** By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], 11, 575—576).—The *acetate* forms tangled, deliquescent crystals, and is insoluble in ether. It dissociates in a dry atmosphere. The heat of formation (sol.) is +1.7 Cal. The *amidoacetate* forms large, brilliant, transparent crystals, and is anhydrous. The heat of formation (sol.) is 0.8 Cal. The *hydrogen malonate*,  $\text{C}_3\text{O}_4\text{H}_4\cdot\text{CON}_2\text{H}_4$ , forms large, transparent crystals, and is anhydrous. The heat of formation (sol.) is +2.5 Cal. The normal malonate could not be prepared. The *glycollate* is crystalline, and insoluble in ether. The heat of formation (sol.) is +2.0 Cal. All the above salts are completely dissociated in aqueous solution.

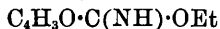
The ureides of acetic and amidoacetic acids cannot be formed by direct dehydration of the salts, as the reaction is endothermic; the reverse is the case with the malonate and glycollate.

JN. W.

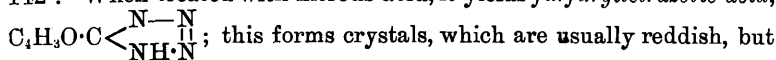
**Hydrate of Uric acid.** By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], 11, 571—573).—The heat of formation of dipotassium urate from the acid and dilute potash is +6.5 Cal., and the heat of liberation of the acid from this salt by hydrochloric acid is +21.5 Cal. From these data it follows that the heat of neutralisation of crystallised uric acid is 0.8 Cal. greater than that of precipitated uric acid. Fritzsché's view that the voluminous precipitate liberated by hydrochloric acid from a borax solution of pure uric acid is identical with the crystalline dihydrate obtained in a similar manner from snakes' excrement is therefore confirmed.

JN. W.

**Action of Hydrazine on Furfurimido-ether.** By ADOLF PINNER and N. CARO (*Ber.*, 1895, 28, 465—473; compare *Abstr.*, 1894, i, 385).—Powdered hydrazine sulphate (1 mol.) is added to the calculated quantity of 33 per cent. caustic potash, furfurimido-ether,

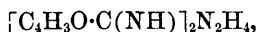


(1 mol.), is then added, and a little alcohol; after 24 hours, the mixture yields *furfurylhydrazidine*,  $\text{C}_4\text{H}_3\text{O}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}_2$ , an oil which solidifies within 12 hours, but then contains some products of decomposition; the *picrate* melts at 164°, and the *benzylidene* compound at 142°. When treated with nitrous acid, it yields *furfuryltetrazotic acid*,



colourless when pure; it melts at 199°, at the same time turning red and decomposing; the *ammonium* salt melts and decomposes at 118°.

If a mixture of the imido-ether with hydrazine, in the proportion of 2 :  $1\frac{1}{2}$  mols., is left for 4—5 days, *difurfurylhydrazidine*,



is formed. This crystallises in yellow prisms and melts at  $185^\circ$ ; the *platinochloride* darkens at  $170^\circ$  and melts and decomposes at  $238^\circ$ . Nitrous acid converts it into *furoylfurfurylhydrazidine*,

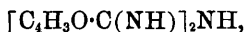


this loses water at  $120^\circ$ , forming the triazole. When *difurfurylhydrazidine* is boiled for half an hour with glacial acetic acid, it yields *difurfuryltriazole*,  $C_4H_3O \cdot C \begin{smallmatrix} N \\ \text{---} \\ NH \cdot N \end{smallmatrix} C \cdot C_4H_3O$ , which melts at  $185^\circ$ , and yields an *acetyl* derivative melting and decomposing at  $120^\circ$ ; it then solidifies, and melts again at  $185^\circ$ .

If the imido-ether and hydrazine, in the proportion of 1 :  $1\frac{1}{2}$  mols., are allowed to remain overnight, the mixture filtered, and the filtrate heated on the water bath, *difurfuryldihydrotetrazine*,



is obtained; it forms yellow needles, reddens on exposure to air, and melts and reddens at  $208^\circ$ ; the *diacetyl* derivative melts at  $197^\circ$ . It is oxidised on exposure to the air, or by ferric chloride, yielding *difurfuryltetrazine*,  $C_4H_3O \cdot C \begin{smallmatrix} N & N \\ \text{---} & \text{---} \\ N & : & N \end{smallmatrix} C \cdot C_4H_3O$ , which crystallises in red needles, melts at  $195^\circ$ , and is easily reduced to the dihydro-compound. It is converted, by boiling with strong hydrochloric acid, into *difurfurylisodihydrotetrazine*,  $C_4H_3O \cdot C \begin{smallmatrix} N \cdot NH \\ \text{---} \\ NH \cdot N \end{smallmatrix} C \cdot C_4H_3O$ , which melts at  $245^\circ$ , and yields a *diacetyl* derivative melting at  $166^\circ$ . If the mixture of imido-ether and hydrazine is at once filtered and the filtrate allowed to remain for 4—6 weeks, *difurfurylimidine*, probably



is deposited; it is colourless when pure, but is often yellowish, melts at  $200^\circ$ , is a monacid base, and yields only a *diacetyl* derivative, which melts at  $138^\circ$ .

C. F. B.

**Occurrence of Hexanaphthene in Caucasian Naphtha.** By VLADIMIR B. MARKOVNIKOFF (*Ber.*, 1895, **28**, 577—578).—Previous attempts to isolate this compound from Caucasian naphtha have been unsuccessful. A fraction boiling at  $78$ — $80^\circ$  was obtained free from aromatic compounds, having sp. gr. =  $0.756$  at  $15^\circ/15^\circ$ ; this was nitrated, and the portion soluble in potash reduced, when hexamethylenamine was obtained, indicating the presence in the naphtha of hexamethylene (hexanaphthene) in considerable quantity.

J. B. T.

**Oxidation by Incomplete Combustion.** By JOHANN WALTER (*J. pr. Chem.*, 1895, [2], **51**, 107—111).—The author has examined the behaviour of a number of substances when the vapour is mixed

with air and passed over a heated copper spiral, the apparatus being similar to that employed for the preparation of formaldehyde from methylic alcohol. Toluene yields a little benzoic acid, together with benzaldehyde to the extent of 5.7 per cent. of the toluene used up. The best result was obtained by the use of asbestos which had been saturated with ammonium vanadate and ignited; in this case, crystals of impure anthraquinone were also obtained. Phenol, when submitted to the same treatment, yields a little diphenylene oxide. Diphenylamine and methyldiphenylamine yield very small amounts of carbazole and acridine respectively, whilst tolunitrile was obtained from monomethylorthotoluidine.

A. H.

**Freezing Points of some Carbon Compounds.** By RAOUL PICTET (*Compt. rend.*, 1894, **119**, 955—957).—The freezing points of a number of carefully purified carbon compounds were determined, with the precautions previously described.

	Freezing point.		Freezing point.
Benzylic chloride . . . .	−47.9°	Piperidine . . . . .	−17.0°
Benzylidenic chloride .	−17.0	Quinoline . . . . .	−19.5
Benzotrichloride . . . .	−17.0	Propionic acid . . . .	−24.5
Benzaldehyde . . . . .	−13.5	Ortho-xylene . . . .	−45.0
Cinnamaldehyde . . . .	− 7.5		

Toluene, metaxylene, mesitylene, pyridine, methylaniline, isobutyric acid, and lactic acid do not solidify, even at  $-100^{\circ}$ , and their freezing points are still under investigation.

The introduction of the methyl group into the benzene nucleus always lowers the freezing point; compare benzene and toluene, aniline and methylaniline.

The substitution of chlorine for hydrogen in a methyl group that has been introduced into a benzene nucleus raises the freezing point, but this effect ceases after two chlorine atoms have been introduced.

The results also confirm Baeyer's law that in the case of homologous compounds of similar constitution the freezing point rises and falls according as the number of carbon atoms is odd or even.

The more symmetrical the structure of a compound, and the more compact the grouping of the atoms in the molecule, the higher is the freezing point, as compared with other compounds of the same series; for instance, butyric acid solidifies at  $-19^{\circ}$ , but isobutyric acid does not solidify even at  $-100^{\circ}$ , and normal caproic acid solidifies at  $-18^{\circ}$ , whereas isocaproic acid does not solidify at  $-100^{\circ}$ . The three xylenes are examples of the same law.

C. H. B.

**$\alpha$ -Hexachlorophenol.** By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1894, [3], **11**, 557—560).— $\alpha$ -Hexachlorophenol can be prepared by the action of chlorine on phenol in presence of antimonie chloride. The phenol should first be converted into its trichloro-derivative by the action of chlorine alone, and further chlorination effected in presence of the antimonie chloride (4—5 per cent.) at a temperature not exceeding  $125$ — $130^{\circ}$ . The mass becomes solid from formation of

pentachlorophenol, and is converted into the liquid hexachloro-derivative by the continued action of the chlorine. If the chlorination is carried too far, an *octochlorophenol* (*hexachlorophenol dichloride*) is formed.

$\alpha$ -*Hexachlorophenol*,  $C_6Cl_6O$ , after crystallisation from benzene and light petroleum, melts at  $107^\circ$ . JN. W.

**Bromine Derivatives of Paraisobutylphenol.** By FRANK B. DAINS and I. R. ROTHROCK (*Amer. Chem. J.*, 1895, **17**, 113—114).—*Bromoparaisobutylphenol*, prepared by the action of bromine (1 mol.) on the phenol or its sodium salt, crystallises in fan-like clusters of blunt needles, melts at  $50^\circ$ , and is easily soluble in ordinary organic solvents. The *benzoate* yields needles melting at  $78.5^\circ$ . When 2 mols. of bromine or an excess is used, *dibromoparaisobutylphenol* is formed. It crystallises in large, yellow plates, melts at  $78^\circ$ , and is readily soluble in organic solvents. L. T. T.

**Identity of Liebmann's Isoamylphenol with Tertiary Amylphenol.** By RICHARD ANSCHÜTZ and H. BECKERHOFF (*Ber.*, 1895, **28**, 407—410).—The tertiary amylphenol of B. Fischer and Grützner (*Abstr.*, 1893, 563) is shown to be identical with the isoamylphenol of Liebmann (*Abstr.*, 1882, 171, 727). The former boils at  $127.6^\circ$  under 12 mm. pressure, the latter at  $130.6^\circ$  under 12 mm.; both melt at  $93^\circ$ , and are identical in appearance. Both yield an identical *benzoate* (compare Kreysler, *Abstr.*, 1885, 1055), which melts at  $60^\circ$  (not  $80.5$ — $81^\circ$ ), boils at  $205^\circ$  under 11 mm. pressure, and crystallises in the rhombic system;  $a:b:c = 0.7209:1:0.8841$ ;  $2E = 61^\circ 30'$  (Li);  $62^\circ 11'$  (Na);  $56^\circ 59'$  (Ti). The two substances are therefore identical; probably it is *tertiary amylphenol*. C. F. B.

**Nitration of Organic Bases.** By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 399—403).—This nitration in the side chain can be effected by means of nitric anhydride, but also by the dehydrating action of acetic anhydride on the nitrate of the base; the resulting nitramine ("diazoacid") is converted by mineral acids into a nitro-derivative of the base; for example,



As regards the yield of nitramine, it is greatest—from 75 per cent. of the base downwards—in the case of ortho- and para-nitro-derivatives, least in the case of bases which, like aniline and toluidine, contain no negative substituting group. The following compounds were prepared; the temperatures given are melting points.

*Phenylnitramine*,  $C_6H_5 \cdot NH \cdot NO_2$ . *Tolynitramines*, 1:4, white nacreous plates,  $52^\circ$ ; 1:2, colourless oil. *Nitrophenylnitramines*, 1:4, yellow, silky needles,  $111$ — $112^\circ$ ; 1:3, yellow needles,  $86$ — $87^\circ$ ; 1:2, lustrous, yellow needles, with sweet taste,  $65.5^\circ$ . *Metanitroparatolynitramine*, lustrous yellow needles,  $79$ — $80^\circ$ . *Metanitroorthotolynitramine*, lustrous yellow needles,  $103^\circ$ . *Parachlorophenylnitramine*, lustrous white needles,  $107$ — $108^\circ$ . *Parabromophenyl-*

*nitramine*, silky white needles, 101·5—102°. *Pseudocumylnitramine*,  $[\text{Me}_3 : \text{NH} \cdot \text{NO}_2 = 1 : 3 : 4 : 5]$ , white nacreous needles, 86·5—87°.

C. F. B.

**Phenylethylenediamine.** By FRANZ FEIST and HUGO ARNSTEIN (*Ber.*, 1895, **28**, 425—427; compare A. Purgotti, *Gazzetta*, 1894, ii, 427).—Phenylethylenediamine is obtained by reducing phenylglyoxime with sodium and alcohol. It is a yellow liquid which boils at 243—246°, and absorbs carbonic anhydride more readily than does diphenylethylenediamine. The *carbamate* is a white powder which melts and evolves gas at 155°; the *picrate* forms yellow crystals which melt at 160°. The *dibenzoyl* derivative melts at 217°, and yields a *trinitro*-derivative melting at 117°.

M. O. F.

**Theory of Diazo-compounds.** By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 444—449).—The author holds the view that in diazo-salts the nitrogen atom to which a negative ion is attached must be regarded as quinquevalent. According to this hypothesis, the conversion of diazo- into isodiazo-compounds depends on the transformation of the radicle “phenylazonium” ( $\text{N}:\text{NPh}^+$ ) into the “phenylazo”-radicle ( $\cdot\text{N}:\text{NPh}$ ), in consequence of a more positive ion replacing a negative group. Phenylazonium is, therefore, a positive radicle occurring in normal diazo-salts, normal diazo-hydrates, and in Hantzsch’s unstable potassium benzenediazosulphonate; the stable salt contains the phenylazo-radicle, which is also present in azo- and diazoamido-compounds, and in the isodiazo-hydrates and their salts.

M. O. F.

**The Isomeric Diazobenzene Potassium Sulphites.** By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], **51**, 80—90; compare Abstr., 1894, i, 597).—A polemical paper dealing with the theory of the constitution of these compounds proposed by Hantzsch. (See also this vol., i, 25, 180.)

A. H.

**Action of Ethylic Cyanacetate on Mononitrodiazobenzene Salts.** By PAUL W. UHLMANN (*J. pr. Chem.*, 1895, [2], **51**, 217—234).—In order to investigate the influence of substituent groups on the isomerism of the compounds obtained by Krückeberg (Abstr., 1894, i, 369), the author has examined the products of the action of ethylic cyanacetate on the three nitrodiazobenzene chlorides.

The compounds obtained exhibit relations similar to those previously described.

Metanitrodiazobenzene chloride yields the  $\alpha$ -condensation product as a dark yellow, crystalline powder, which, after recrystallisation from benzene, forms dark brown, lustrous needles, and melts at 136—137°. When it is melted, it passes into the  $\beta$ -derivative, which may also be obtained by decomposing the potassium salt with carbonic anhydride, as a light brown, microcrystalline powder melting at 124—125°. Only one potassium salt appears to be formed; it crystallises in light brown needles, and, when decomposed by hydrochloric acid, yields the  $\alpha$ -derivative, whilst the  $\beta$ -derivative is precipitated by carbonic anhydride. The sodium salt crystallises in plates of the same colour as the crystals of the potassium salt. Ethylic iodide reacts with the



potassium salt to form an *ethyl* derivative, which crystallises in long, silky needles melting at 148—149°. Benzoic chloride produces the *benzoyl* derivative which forms almost white, lustrous plates melting at 174—175°. Carbonyl chloride reacts with 2 mols. of the potassium salt to form a substance which melts at 141—142°. When the ethyl derivative is heated with hydrochloric acid at 120—130°, it yields metanitroethylaniline, so that the stable ( $\beta$ ) condensation product must be considered as a hydrazone.

The  $\alpha$ -derivative of paranitrodiazobenzene chloride forms slender, pale yellow needles melting at 170—172°, whilst the  $\beta$ -derivative, obtained in a manner similar to the corresponding meta-compound, melts at the higher temperature of 184°, and is a light yellow, granular powder. The potassium salt could not be obtained pure, but forms a violet-red solution. The  $\alpha$ -condensation product of orthonitrodiazobenzene chloride crystallises in scale-like forms and melts at 116°. When heated to 160°, it is converted into the  $\beta$ -modification, which crystallises in large, monosymmetric prisms melting at 146°. The potassium salt forms a dark red solution, and crystallises in violet-brown plates with a metallic lustre. The isomeric modifications of all three derivatives also differ in solubility in benzene. A. H.

**Explosiveness of 1:4-Nitrodiazobenzene Nitrate.** By EUGEN BAMBERGER (*Ber.*, 1895, 28, 538—539).—This substance on one occasion unaccountably exploded with terrible consequences, when it was being brushed along with a porcelain spatula. Generally speaking it is much less explosive than diazobenzene, and has many times been rubbed on a porous tile without exploding. 1:4-Nitroisodiazobenzenehydroxide is also explosive, but less violently so.

C. F. B.

**Diazobenzene Aniline Chloride.** By J. H. KASTLE and B. C. KEISER (*Amer. Chem. J.*, 1895, 17, 91—98).—When attempting to obtain diazobenzene chloride by the action of nitrosyl chloride on aniline hydrochloride, the double salt *diazobenzene aniline chloride*,  $N_2PhCl, NH_3PhCl$ , was obtained in the form of well-defined needles which turned green, then pink, and finally brown, when exposed to the air. This salt dissolves freely in alcohol, and in water, yielding green solutions which change to red on boiling or exposure to air. It explodes a little above 105°, and when boiled with water, it evolves two-thirds of its nitrogen and forms phenol and aniline hydrochloride. When reduced with stannous chloride, it yields phenylhydrazine and aniline hydrochloride, and when treated with potash, diazoamidobenzene is formed. It yields a platinumchloride,  $N_2PhCl, NH_3PhCl, PtCl_4$ .

L. T. T.

**Synthesis of Aromatic Hydrazines from Hydrazine Hydrate.** By ATTILIO PURGOTTI (*J. pr. Chem.*, 1895, [2], 51, 111—112).—The author draws attention to the fact that he described the preparation of 2:4-dinitro- and 2:4:6-trinitro-phenylhydrazine from hydrazine hydrate (this vol., i, 27) before the publication of the paper in which Curtius and Dedichen (this vol., i, 29) described the preparation of the same compounds by the same method.

A. H.

**Acid Hydrazides and Azides.** By THEODOR CURTIUS (*Ber.*, 1895, **28**, 522—523).—In connection with Wolff's recent communication on compounds from acid hydrazides and sugars (this vol., i, 216), the author points out that the first of these substances, arabinose-nitrobenzoylhydrazide, was prepared by Radenhausen, and that he himself, and not Struve, prepared and described benzoylhydrazide in 1890. He desires to reserve the acid hydrazides and azides for further uninterrupted investigation. J. B. T.

**Mononitrobenzoylhydrazines.** By THEODOR CURTIUS and O. TRACHMANN (*J. pr. Chem.*, 1895, [2], **51**, 165—179; compare this vol., i, 32).—*Methylic orthonitrobenzoate* is a yellow liquid which has an odour of strawberries, and boils at 275°; a similar odour has been ascribed to the meta-compound, but when pure this has no odour.

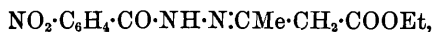
*Orthonitrobenzoylhydrazine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , is obtained by the interaction of methylic orthonitrobenzoate, with the calculated quantity of hydrazine hydrate; it crystallises in large, long, yellow prisms, melts at 123°, and dissolves somewhat freely in alcohol and water, but not in ether, &c.; it reduces Fehling's solution and ammoniacal silver nitrate very quickly; dilute mineral acids decompose it into its parent compounds. *Metanitrobenzoylhydrazine*, similarly prepared, crystallises in yellow needles, melts at 152°, and is less soluble than the ortho-compound, which it otherwise resembles. *Paranitrobenzoylhydrazine* crystallises in slender, yellow needles, melts at 210°, and is less soluble than the other two isomerides, which it resembles in chemical behaviour. The *sodium* derivatives,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NNa}\cdot\text{NH}_2$ , and the *hydrochlorides*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ , of the three isomerides are described.

*Benzylidene-ortho-, -meta- and -para-nitrobenzoylhydrazine*,



prepared by the interaction of benzaldehyde and the nitrobenzoylhydrazines, are described; they melt at 152°, 203°, and 247°, respectively. With acetone, the nitrobenzoylhydrazines yield *acetone-nitrobenzoylhydrazines*,  $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ; the *ortho*-derivative forms yellow crystals, and melts at 205°; the *meta*-derivative small, yellow crystals, and melts at 152°; the *para*-derivative crystallises in greenish-yellow needles; they dissolve in alcohol.

The *ethylic nitrobenzoylhydrazoacetoacetates*,



are obtained by the interaction of the nitrobenzoylhydrazines with ethylic acetoacetate; the *ortho*-derivative crystallises in lustrous, yellow prisms, melts at 113°, and dissolves freely in alcohol and chloroform; the *meta*-derivative forms small, white crystals, melts at 106°, and dissolves freely in alcohol; the *para*-derivative is rather more difficult to prepare, and crystallises in aggregates of yellow needles, freely soluble in alcohol.

*Dinitrodibenzoylhydrazines*,  $\text{N}_2\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , are formed by heating the ethylic nitrobenzoylhydrazine acetoacetates above their melting points, or by dissolving them in dilute alkalis, and warming the

solutions with an excess of acid. The *di-ortho*-compound crystallises in slender, white needles or laminae, melts above  $250^{\circ}$ , and is freely soluble in hot glacial acetic acid; the *di-meta*-compound crystallises in white laminae or needles, melts at  $242^{\circ}$ , and is freely soluble in hot glacial acetic acid; the *di-para*-compound forms yellowish, slender needles, melts above  $245^{\circ}$ , and is also freely soluble in hot glacial acetic acid. The dinitrodibenzoylhydrazines are soluble without appreciable decomposition in solutions of the alkalis, and if the calculated quantities be employed alkali derivatives are obtained. They show no tendency to form nitroso-derivatives or acetyl derivatives; acids convert them into nitrobenzoic acids and hydrazine salts.

A. G. B

**Imido-derivatives of Carbonic acid.** By FELIX LENGFELD and JULIUS STIEGLITZ (*Amer. Chem. J.*, 1895, **17**, 98—113).—*Bromo-formanilide*,  $\text{NPh}\cdot\text{COBr}$ , was formed by passing dry hydrogen bromide over phenylic isocyanate. It forms white crystals, melts at  $67^{\circ}$ , and decomposes into its components at  $85\text{--}100^{\circ}$ . Hydrogen chloride appears to be without action on bromo-formanilide, and hydrogen bromide without action on chloro-formanilide. *Phenylimidocarbonyl bromide*,  $\text{NPh}\cdot\text{CBR}_2$ , was prepared by the action of bromine on phenylic isocyanide. It is an oil boiling at  $127^{\circ}$  under 18 mm. pressure. When treated with sodium ethoxide, it yields *ethylic phenylimidobromoformate*,  $\text{NPh}\cdot\text{CBr}\cdot\text{OEt}$ , which decomposes on boiling and is less stable than the corresponding chloro-derivative. When acted on by hydrochloric acid, it mainly yields chloro-formanilide and ethylic bromide, although a small quantity of bromo-formanilide and ethylic chloride is produced, and a very similar product is yielded by the action of hydrogen bromide on ethylic phenylimidochloroformate. The constitution of the intermediate additive compounds probably formed is discussed, but the authors did not succeed in isolating them. When, however, phenylic phenylimidochloroformate is treated with hydrogen chloride, the additive product *phenoxyformophenylamido-dichloride*,  $\text{OPh}\cdot\text{CCl}_2\cdot\text{NPh}$ , can be isolated as a white substance softening at  $60^{\circ}$  and melting at  $65^{\circ}$ . In the presence of moisture, it forms phenyl carbanilate.

When carbodiphenylimide is treated with hydrogen chloride, the hydrochloride  $\text{C}(\text{NPh})_2\cdot\text{HCl}$  (m. p.  $92\text{--}95^{\circ}$ ) is first formed, and then *carbodiphenylimide dihydrochloride*,  $\text{C}(\text{NPh})_2\cdot 2\text{HCl}$ . This crystallises in tetragonal or orthorhombic prisms, and begins to melt and decompose at  $130^{\circ}$ , apparently leaving a carbodiphenylimide. When boiled with water, it gives carbanilide.

When chloro-formodiphenylamidine,  $\text{NHPH}\cdot\text{CCl}\cdot\text{NPh}$ , is treated with sodium ethoxide, ethoxyformodiphenylamidine,  $\text{NHPH}\cdot\text{C}(\text{OEt})\cdot\text{NPh}$ , is formed, and this with hydrogen chloride yields ethylic chloride and carbanilide  $\text{CO}(\text{NHPH})_2$ .

The results show that when hydrogen chloride is taken up by acid derivatives of the formula  $\text{OR}\cdot\text{CX}\cdot\text{NPh}$  or  $\text{Y}''\cdot\text{C}\cdot\text{NPh}$ , containing the phenylimido-group, the double linking is severed and the group  $\cdot\text{CCl}\cdot\text{NHPH}$  formed.

L. T. T.

**Action of Sodium Ethoxide on Carbodiphenylimide.** By JULIUS STIEGLITZ (*Ber.*, 1895, **28**, 573—574).—*Ethylisocarbanilide*

(ethylic phenylimidocarbanilate),  $\text{HNPh}\cdot\text{C}(\text{NPh})\cdot\text{OEt}$ , is prepared by the interaction of carbodiphenylimide and sodium ethoxide in alcoholic solution at  $-5^\circ$ ; it is a colourless mobile liquid, boiling at  $182^\circ$  (10 mm.), the refractive index = 1.6028 at  $20^\circ$ . The yield is practically quantitative. From the production of similar compounds to the above by the action of sodium ethoxide on carbodiphenylimide chloride, the author and F. Lengfeld (preceding abstract) recently concluded that the latter compound has the formula  $\text{HNPh}\cdot\text{CCl}\cdot\text{NPh}$ ; this now requires confirmation or revision, and the subject is being further investigated.

J. B. T.

**Constitution of Rosaniline.** By LOTHAR MEYER (*Ber.*, 1895, 28, 519—522).—Referring to Weil's paper on the constitution of triphenylmethane derivatives (this vol., i, 234), the author points out that a photometric investigation of the products formed by the action of hydrochloric acid on magenta has been in progress under his direction for more than 10 years. With hydrochloric acid, aqueous or alcoholic, in excess, yellowish red hydrochlorides are formed; when diluted, these change successively to colourless compounds, and finally to blue-red magenta. These results are in better accord with Rosenstiehl's formula for rosaniline than with E. and O. Fischer's, which indicates the presence of a quinoidal linkage (compare Abstr., 1893, i, 464). If the first formula is correct, then the yellowish-red compound is probably the chloride  $\text{CCl}(\text{C}_6\text{H}_4\cdot\text{NH}_2, \text{HCl})_3$ , the colourless substance is the carbinol  $\text{HO}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2, \text{HCl})_3$ , and the blue-red one the chloride  $\text{CCl}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3$ . The subject is being further investigated in various directions. A number of crystalline ethers has been prepared from triphenylbromomethane and metallic alkyl oxides, and will be described later.

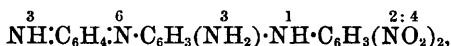
J. B. T.

**Preparation of Condensation Products from Chloroform and Benzene.** By GUSTAV WENDT (*J. pr. Chem.*, 1895, [2], 51, 344—346).—The amount of condensation product obtained in the preparation of flavaniline from acetanilide and of triphenylmethane from chloroform and benzene is largely increased by the addition of kieselguhr, whilst sand has no marked effect on the yield.

A. H.

**Constitution of the Safranines.** By GEORGE F. JAUBERT (*Ber.*, 1895, 28, 508—513; compare this vol., i, 219).—Dinitrodimethylmetamidodiphenylamine,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , is prepared from 1 : 2 : 4-chlorodinitrobenzene and metamidodimethylaniline hydrochloride; it crystallises from alcohol in garnet-red plates, and melts at  $136$ — $137^\circ$ . The nitroso-derivative is deposited in scarlet flocks. Dinitrotetramethylsafranine is prepared by the oxidation of a mixture in molecular proportion of dinitrodimethylmetamidodiphenylamine and paramidodimethylaniline sulphate, a blue compound is first formed, which when heated is converted into the safranine.

*Dinitrophenylphenylene-blue,*



is obtained in a similar manner from dinitrometamidodiphenylamine

and phenylenediamine hydrochloride, as a blue, crystalline powder with a coppery reflex; it is insoluble in water, is readily converted into the safranine when exposed to air in alcoholic solution, explodes when heated and decomposes and becomes yellow by the action of mineral acids.

The *safranine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_3 \cdot \text{NH} \\ | \\ \text{N} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \end{smallmatrix}$ , is prepared by heating the preceding indamine in alcoholic solution. The *hydrochloride* dissolves in water and alcohol with a carmine, in concentrated hydrochloric acid with a sky blue, and in concentrated sulphuric acid with a green coloration; with cotton mordanted with tannin, it gives a bluer lustre than "safranine T," and is deposited in greenish lustrous crystals. The *diazo-derivative* is violet-blue.

The formation of safranines as described above, resembles the conversion of tolylene-blue into tolylene-red which contains two amido-groups and the complex  $< \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} >$ , whilst the safranines probably contain a quinoidal linkage; it is to this that the difference in their behaviour, especially in their basic properties, is due. That phenosafranine does not contain two amido-groups is proved by its yielding in aqueous solution a monodiazo-derivative only, not a tetrazo-compound like tolylene-red, therefore it cannot be an ammonium base. Safranide, formed by boiling diazophenosafranine in alcoholic solution, yields no diazo-compound, it therefore contains no amido-group, and cannot be an ammonium base. J. B. T.

#### Orthocoumaraldehyde Methyl Ether from Oil of Cassia.

By JULIUS BERTRAM and RUDOLF KÜRSTEN (*J. pr. Chem.*, 1895, [2], 51 316—325).—Oil of Cassia often yields a crystalline product on rectification. This consists of *orthocoumaraldehyde methyl ether*,



and forms large, faintly yellowish crystals which melt at 45—46°. It boils at 160—161° (12 mm.) and decomposes very readily when exposed to light and air. The *phenylhydrazone* forms pale yellow crystals melting at 116—117°, and the *oxime* crystallises in colourless matted needles melting at 125—126°. The constitution of the aldehyde follows from the facts, that when fused with potash it is converted into salicylic acid, that it is oxidised by potassium permanganate to methylsalicylic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , and that silver oxide converts it into  $\beta$ -methylcoumaric acid,  $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$ , melting at 182—183°. It can readily be prepared synthetically by the condensation of methylsalicylaldehyde with acetaldehyde.

$\beta$ -Methylcoumaric acid undergoes polymerisation when exposed to light, an acid which has a molecular weight of 356 and which melts at 260—262° being formed. Cinnamic acid also undergoes partial polymerisation under the same circumstances, an acid which melts at 274°, and is probably identical with Liebermann's  $\alpha$ -truxillic acid, being formed. A. H.

**Dihydromethylcoumaran.** By CARL D. HARRIES and GEORGE J. BUSSE (*Ber.*, 1895, 28, 501—503).—Methyl orthohydroxystyrylketone

(methylorthocoumaroketone),  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COMe}$ , prepared from salicylaldehyde and acetone, yields *methyl orthohydroxydihydrostyryl ketone* (methyldihydrocoumaroketone),  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , not methylorthocoumaryl alcohol,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CHMe}\cdot\text{OH}$ , as previously stated (Abstr., 1892, 169). The *phenylhydrazone* melts at  $123\text{--}124^\circ$ . The ketone, when reduced with zinc and hydrochloric acid, is converted into *dihydromethylcoumaran*,  $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}-\text{CHMe}$ , a

derivative of the complex  $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}:\text{O}-\text{CH}$ , for which the name *coumaran* is proposed. It is a colourless highly refractive liquid with a pleasing smell, readily miscible with ordinary media, boils at  $223\text{--}226^\circ$  (76 mm.), and gives a red coloration with sulphuric acid.

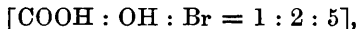
J. B. T.

**Reactions of Amidobenzoic acids.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1895, 120, 100—101).—Alkali hypochlorites produce, with orthoamidobenzoic acid, a red coloration; with the *meta*-acid a red-brown; with the *para*-acid an orange-red; alkali hypobromites produce a bright orange-red colour with all three acids. Alkali hypoiodites give an orange-red with the *ortho*-acid, deep orange or yellow with the *meta*-acid, bright orange or yellow with the *para*-acid; calcium hypochlorite with the *ortho*-acid produces a deep violet coloration which rapidly becomes black or dark green; with the *meta*-acid and the *para*-acid it gives a yellowish-brown coloration. Ferric chloride in very dilute solution gives with the *ortho*-acid a rose colour which changes to wine-red; with the *meta*-acid an amber-yellow, and with the *para*-acid a red-brown colour.

The nitrobenzoic acids give no reactions with these reagents. The reactions with the amido-acids are much more rapid and sensitive than those previously described (Abstr., 1892, 847, 1380; 1893, i, 413, 465, 641).

C. H. B.

**Action of Bromine on Phenylc Salicylate, Phenylc Benzoate, Ortho-, Meta-, and Para-Cresylic Benzoate, and Guaiacol Benzoate.** By P. KAUSCHKE (*J. pr. Chem.*, 1885, [2], 51, 210—213).—Phenylc bromosalicylates are produced by the direct bromination of salol, but the tribromo-derivative in small quantity only unless the reaction be conducted at  $100^\circ$ , under pressure, and in the presence of iodine or ferric chloride. The monobromosalicylate,



melts at  $111.5^\circ$ , and its *amide* at  $232^\circ$ . The dibromosalicylate,  $[\text{COOH} : \text{OH} : \text{Br}_2 = 1 : 2 : 3 : 5]$ , melts at  $126^\circ$ , and its *amide* at  $170^\circ$ . These have been described before.

*Phenylc tribromosalicylate*,  $[\text{COOH} : \text{OH} : \text{Br}_3 = 1 : 2 : 3 : 5 : ?]$ , crystallises in long needles, melts at  $192^\circ$ , and dissolves in chloroform and glacial acetic acid; its *amide* melts at  $97^\circ$ . *Bromophenylc tribromosalicylate*,  $\text{OH}\cdot\text{C}_6\text{HBr}_3\cdot\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$ , crystallises in needles, melts at  $164^\circ$ , and is sparingly soluble in glacial acetic acid and in chloroform.

Bromophenylic benzoate is the product of the action of bromine (1 or 2 mols.) on phenylic benzoate (1 mol.); it melts at  $102^{\circ}$ . By the action of a larger proportion of bromine, the compound  $C_{12}H_3Br_7O_4$  is formed; this crystallises in golden laminae, melts at  $260^{\circ}$ , and is sparingly soluble; it is reduced by sulphurous acid to a white substance of the formula  $C_{12}H_3Br_7O_4$ , indicating its probable quinonoid character.

*Bromorthocresylic benzoate* melts at  $59^{\circ}$ ; *bromometacresylic benzoate* at  $82^{\circ}$ ; *bromoparacresylic benzoate* is a yellow oil which solidifies to long needles, below  $0^{\circ}$ . *Bromoguiacol benzoate* crystallises in colourless prisms and melts at  $76-78^{\circ}$ .  
A. G. B.

**Cadmium Salicylate.** By P. CÉSARIS (*L'Orosi*, 17, 262—265).—*Cadmium salicylate*,  $(C_7H_5O_3)_2Cd$ , prepared by ordinary methods, using the acid and cadmium oxide or carbonate, is obtained in lustrous crystals melting at  $300^{\circ}$ ; it is sparingly soluble in water, but more soluble in alcohol, ether, or glycerol. The salt possesses valuable antiseptic properties.  
W. J. P.

**Phenyl- $\alpha$ -amidolactic acid (Phenylserine).** By EMIL ERLMAYER, jun., and ERNST FRÜSTÜCK (*Annalen*, 1895, 284, 36—49; compare Abstr., 1893, i, 166).—Among the condensation products obtained from benzaldehyde and glycocine in presence of sodium hydroxide, is the *sodium* salt of  $\alpha$ -benzylideneamidophenyllactic acid,



The acid itself has not been isolated, but its *acetyl* derivative crystallises in needles and melts at  $169-170^{\circ}$ .

Anhydrous phenyl- $\alpha$ -amidolactic acid decomposes below  $190^{\circ}$ ; the hydrated acid, which contains  $1H_2O$ , melts at  $193-194^{\circ}$  with decomposition. The *copper* salt is violet. Benzoic anhydride converts phenylamidolactic acid into the lactimide of benzoylamidocinnamic acid,  $CHPh:C \begin{smallmatrix} CO \\ | \\ NBz \end{smallmatrix}$ , which is also obtained by condensing benzaldehyde with hippuric acid. The lactimide,  $CHPh:C \begin{smallmatrix} CO \\ | \\ NAc \end{smallmatrix}$ , produced

by the action of acetic anhydride on phenyl- $\alpha$ -amidolactic acid, crystallises from alcohol in white needles which melt at  $146-147^{\circ}$ ; it is also obtained by the condensation of benzaldehyde with glycocine in presence of acetic anhydride. When the solution of the lactimide in sodium hydroxide is acidified, the *acetyl* derivative of  $\alpha$ -amidocinnamic acid is formed; it crystallises from water and contains  $2H_2O$ . The hydrated acid melts at  $185-186^{\circ}$ , and the anhydrous substance melts and evolves gas at  $190-191^{\circ}$ .  
M. O. F.

**Nitrophenylglycidic acids.** By ALFRED EINHORN and ALFRED GERNSHEIM (*Annalen*, 1895, 284, 132—153; compare Eichengrün and Einhorn, Abstr., 1890, 1128).—The acid obtained (*loc. cit.*) on oxidising orthonitrometachlorophenyl- $\beta$ -lactaldehyde and orthonitrometachlorophenylhydroxyethyl methyl ketone melts at  $156^{\circ}$ . It was

at first supposed that this acid was nitrochlorophenyl- $\beta$ -lactic acid, but the results of the author's experiments now show that on oxidising a substituted phenyllactaldehyde or methyl ketone with sodium hypochlorite, the corresponding phenylglycidic acid is formed. The acid (m. p.  $156^{\circ}$ ) prepared from nitrochlorophenylhydroxyethyl methyl ketone is, therefore, the nitrochlorophenylglycidic acid,

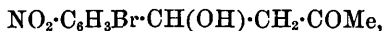
$$O < \begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NO}_2 \\ \text{CH} \cdot \text{COOH} \end{array}$$

By means of this reaction, orthonitrophenylglycidic and 3:6-bromonitrophenylglycidic acids have been prepared.

Metabromobenzaldehyde forms an *oxime* which melts at  $71.5^{\circ}$ ; the *phenylhydrazone* melts at  $141-142^{\circ}$ .

3:6-Bromonitrobenzaldehyde crystallises from alcohol in long, pale yellow needles, and melts at  $74^{\circ}$ ; it dissolves in hot water, and is volatile in an atmosphere of steam. The *phenylhydrazone* forms dark red needles which melt and decompose at  $180^{\circ}$ ; the *oxime* crystallises from water in pale yellow needles, and melts at  $113^{\circ}$ .

3:6-Bromonitrophenylhydroxyethyl methyl ketone,



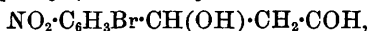
is prepared by the action of aqueous soda on a solution of bromonitrobenzaldehyde in acetone. It crystallises from alcohol in lustrous plates, and melts at  $101-102^{\circ}$ ; alkalis convert it into dibromindigo, and the solution in concentrated sulphuric acid is red.

3:6-Bromonitrophenylglycidic acid is obtained by agitating the foregoing compound with an aqueous solution of sodium hypochlorite at  $70-80^{\circ}$ . It crystallises from dilute alcohol in small, lustrous, pale yellow plates which melt at  $156^{\circ}$ ; at this temperature, the substance decomposes and becomes blue, owing to the formation of dibromindigo. The *potassium* salt crystallises from dilute alcohol in lustrous needles; the *barium* and *calcium* salts crystallise from hot water.

3:6-Bromonitrocinnamic acid is formed when bromonitrobenzaldehyde is heated with acetic anhydride and anhydrous sodium acetate for 7-8 hours at  $140-150$ . It crystallises in lustrous needles and melts at  $171^{\circ}$ ; the solution in concentrated sulphuric acid is green. The *silver* salt is crystalline.

3:6-Bromonitrophenyl- $\alpha$ -chlorolactic acid is obtained by treating the potassium salt of the foregoing acid with sodium hypochlorite; it melts at  $147-148^{\circ}$ . Alcoholic potash converts it into bromonitrophenylglycidic acid.

3:6-Bromonitrophenyl- $\beta$ -lactaldehyde,



is prepared by agitating a solution of bromonitrobenzaldehyde in acetaldehyde with aqueous soda; it crystallises with 1 mol. acetaldehyde, which is lost at  $87^{\circ}$ . This compound melts and becomes green at  $92-93^{\circ}$ ; alkalis convert it into dibromindigo. The *phenylhydrazone* crystallises from alcohol in dark red needles, and melts at  $201^{\circ}$ . Sodium hypochlorite oxidises the aldehyde to bromonitrophenylglycidic acid, whilst silver oxide converts it into 3:6-bromonitrophenyl- $\beta$ -lactic acid. This crystallises from hot water in slender silky needles, and melts at  $152^{\circ}$ ; the *silver* salt is crystalline and



the copper salt forms dark blue needles. The ethylic salt separates from light petroleum in large crystals, and melts at  $74.5^{\circ}$ .

M. O. F.

**Acetylgallic and Acetyldibromogallic acids.** By PAUL SISLEY (*Bull. Soc. Chim.*, 1894, [3], 11, 563—568).—Dry acetic chloride has no action on gallic acid, and the product obtained in presence of a trace of water cannot be purified satisfactorily (compare Biétrix, *Abstr.*, 1894, i, 130). When, however, gallic acid is heated with acetic anhydride, and the partially purified product again subjected to the same treatment, *triacetylgallic acid* is obtained as a white, amorphous substance, which crystallises from boiling toluene in very light, colourless, prismatic needles containing toluene of crystallisation. The anhydrous substance melts at  $151^{\circ}$ . It is insoluble in water, but is slowly hydrolysed by it to diacetylgallic acid. The alcoholic solution does not give a colour reaction with ferric chloride.

*Diacetylgallic acid*, with  $\frac{1}{2}\text{H}_2\text{O}$ , melts at  $162^{\circ}$ . In alcoholic solution it gives a yellow precipitate with ferric chloride, but no colour reaction, so that the presence of at least two phenolic groups in the gallic acid molecule appears to be necessary for this purpose. It does not give precipitates or colorations with lime-water or alkalis, or with uranium nitrate. Attempts to prepare the monacetyl compound were unsuccessful.

*Triacetyldibromogallic acid*, from dibromogallic acid, crystallises from toluene in white, prismatic needles, and melts at  $168^{\circ}$ , not at  $94\text{--}98^{\circ}$ , as stated by Biétrix (*loc. cit.*). It is insoluble in water, but soluble in alcohol, ether, and acetic acid, and is completely hydrolysed by water into dibromogallic and acetic acids. It gives a rose colour with alkalis, but no coloration with ferric chloride.

JN. W.

**Oxidation Products of Isodurene.** By PAUL JANNASCH and MAX WEILER (*Ber.*, 1895, 28, 531—535; compare this vol., i, 130).—The residue left after distilling with steam the product of the oxidation of isodurene with nitric acid has now been examined. The (dibasic) acids obtained from it were converted into their methylic salts; part formed normal salts, part methyl hydrogen salts, and the latter were separated by dissolving them out with potash. Both mixtures of salts were then converted into the acids, which were subjected to sublimation; there were thus obtained, from the first portion, besides  $\alpha$ -isodurylic acid, an acid melting at  $334.5\text{--}335.5^{\circ}$ , and subliming in large, hexagonal prisms, the calcium salt of which crystallises with  $3\frac{1}{2}\text{H}_2\text{O}$ ; from the second portion, besides mesitylenecarboxylic acid, an acid melting at  $297\text{--}298^{\circ}$ , and subliming in prisms; its calcium salt crystallises with  $2\text{H}_2\text{O}$ . Both acids have the constitution  $\text{C}_6\text{H}_2\text{Me}_2(\text{COOH})_2$ ; using V. Meyer's rule for the etherification of aromatic acids, the first acid which yielded a normal methylic salt must be a *dimethylisophthalic acid* [ $\text{Me}_2 : (\text{COOH})_2 = 1 : 2 : 3 : 5$  or  $= 1 : 4 : 2 : 6$ ], whilst the second, which yields a methyl hydrogen salt, must have the constitution  $[1 : 3 : 2 : 5]$  or  $[1 : 3 : 4 : 5]$ , probably the former, since it yields no anhydride; if so it is a *dimethylterephthalic acid*.

C. F. B.

**Ethereal Salts of Anhydro- $\alpha$ -amido-acids: Synthesis of Mercapturic acids.** By FRANZ WEISS (*Zeit. physiol. Chem.*, 1895, **20**, 407—434; compare *Abstr.*, 1893, i, 579, and 1894, i, 87).—The action of phosphorus oxychloride on phenylic hippurate (*loc. cit.*) gives rise to *phenylic anhydrohippurate*,  $C_{15}H_{11}NO_2$ , which melts at  $42^\circ$ ; the *dichloro*-derivative sinters at  $52^\circ$ , and melts at about  $150^\circ$ . *Ethylic anhydrohippurate*, obtained in a similar manner from ethylic hippurate, melts at  $58^\circ$ ; it is volatile in steam, and does not dissolve readily in water. Although indifferent towards soda, it is hydrolysed by hydrochloric acid. The *acetyl* derivative of phenylic hydroxyhippurate (*loc. cit.*) melts at  $171$ — $173^\circ$ .

Phenylic anhydro- $\alpha$ -benzoylamidopropionate melts at  $41$ — $42^\circ$ ; when treated with phosphorus pentachloride, it yields *phenylic  $\alpha$ -benzoylamido- $\alpha$ -chloropropionate*, which melts at  $137^\circ$ . Hot alkalis convert this substance into a mixture of phenol and ammonia with benzoic, hydrochloric, and probably pyruvic acids. When pentachloride of phosphorus acts on phenylic  $\alpha$ -benzoylamidopropionate, the anhydro-compound is produced together with the foregoing substance and a nitrogenous compound which melts at  $220$ — $230^\circ$ .

*Phenylic  $\alpha$ -bromothiophenyl- $\alpha$ -benzoylamidopropionate*,

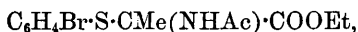


is obtained by acting on phenylic  $\alpha$ -benzoylamido- $\alpha$ -chloropropionate with the sodium derivative of bromothiophenol in alcoholic solution; it melts at  $143^\circ$ , and is hydrolysed by aqueous alkalis. The *amide* crystallises in long needles, and melts at  $201^\circ$ .

*$\alpha$ -Bromothiophenyl- $\alpha$ -benzoyllactimide*,  $C_6H_4Br \cdot S \cdot CMe < \begin{smallmatrix} NBz \\ CO \end{smallmatrix}$ , is

formed during the preparation of the foregoing phenylic salt. It melts at  $153$ — $155^\circ$ , and is not readily hydrolysed by soda; alcoholic ammonia converts it into the amide. M. O. F.

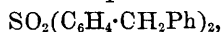
**Derivatives of Bromophenylmercapturic acids.** By SIGMUND FRÄNKEL (*Zeit. physiol. Chem.*, 1895, **20**, 435—442; compare preceding abstract).—*Ethylic bromophenylmercapturate*,



melts at  $91^\circ$ . The *phenylic* salt is obtained by treating a mixture of phenol and mercapturic acid with phosphorus oxychloride; it melts at  $96^\circ$ . The *amide* melts at  $174^\circ$ .

The *benzoyl* derivative of bromophenylcystein melts at  $136^\circ$ ; the *barium* salt crystallises from hot water, the *ethylic* salt melts at  $104^\circ$ , and the *phenylic* salt at  $120^\circ$ . This salt is not identical with phenylic bromothiophenyl- $\alpha$ -benzoylamidopropionate (*loc. cit.*), being geometrically isomeric with it. The *amide* melts at  $191^\circ$ , whilst the isomeride obtained by Weiss from inactive amidopropionic acid melts at  $201^\circ$ . M. O. F.

**Aromatic Sulphones.** By P. GENVRESSE (*Bull. Soc. Chim.*, 1894, [3], **11**, 501—514).—The *sulphone* from *phenylmethane*,



prepared from the sulphone of benzylic bromide and benzene in presence of aluminium chloride, forms colourless, transparent crystals, which soon become opaque, and in air yellow. It is soluble in benzene, sparingly in hot alcohol, and melts at  $162^{\circ}$ . It is not attacked by potash.

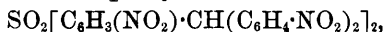
The *sulphone of benzylidene bromide*,  $\text{SO}_2(\text{C}_6\text{H}_4\cdot\text{CHBr})_2$ , obtained from toluenesulphonic acid and bromine at  $170^{\circ}$ , crystallises in colourless, transparent needles. It is soluble in benzene and boiling alcohol, and melts at  $137^{\circ}$ . It is oxidised by permanganate to the sulphone of benzoic acid.

The *sulphone of benzaldehyde*,  $\text{SO}_2(\text{C}_6\text{H}_4\cdot\text{CHO})_2 + 1\frac{1}{2}\text{H}_2\text{O}$ , prepared by the action of water on the preceding compound at  $170$ – $180^{\circ}$ , crystallises in small needles. It is soluble in benzene and alcohol, and melts at  $179^{\circ}$ . By fusion with potash it is converted into the corresponding alcohol and acid derivatives, and these are also obtained by heating the sulphone of benzylic bromide with aqueous lead nitrate. The *sodium hydrogen sulphite compound*, with  $1\frac{1}{2}\text{H}_2\text{O}$ , is voluminous and white; there is also an *ammonia compound*.

The *sulphone of triphenylmethane*,  $\text{SO}_2(\text{C}_6\text{H}_4\cdot\text{CHPh}_2)_2$ , obtained by the action of benzene on the sulphone of benzylidene bromide in presence of aluminium chloride, crystallises from alcohol in small, transparent crystals, which soon become opaque. It is very soluble in benzene and chloroform, and melts at  $68^{\circ}$ .

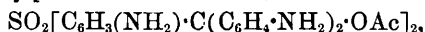
The *sulphone of triphenylcarbinol*,  $\text{SO}_2(\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH})_2$ , is formed by the oxidation of the preceding compound with chromic acid in glacial acetic acid solution. It separates from boiling alcohol in light amber coloured crystals. It is soluble in benzene and acetic acid, and melts at  $78^{\circ}$ .

The *sulphone of trinitrotriphenylmethane*,



is a yellowish substance formed by the action of fuming nitric acid on the sulphone of triphenylmethane. It is soluble in benzene, acetic acid, and alcohol. On oxidation, it yields the corresponding *carbinol*; the yield is 60–70 per cent. of the theoretical. As precipitated by water from acetic acid solution, this is a white substance, soluble in alcohol and benzene, and melting at  $100$ – $110^{\circ}$ .

The *sulphone of pararosaniline acetate*,



is obtained by reducing the trinitrocarbinol with zinc dust in acetic acid solution or with tin and hydrochloric acid, and subsequent treatment with potash and acetic acid. The analytical results were not very satisfactory, probably owing to the presence of the leuco-compound. The acetate separates from acetic acid in green crystals, and, in this solvent, dyes wool, cotton, and silk without a mordant; the green colour is not very bright, but quite fast to soap and light. With potash, it forms a reddish-white precipitate, consisting probably of the free base. The *sulphone of leucopararosaniline*,  $\text{SO}_2[\text{C}_6\text{H}_3(\text{NH}_2)_3\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2]_2$ , formed by reducing trinitrotriphenylmethanesulphone with zinc dust in acetic acid solution, is a colourless, crystalline substance, soluble in alcohol.

*Bi-ethylphenylsulphone*,  $\text{SO}_2(\text{C}_6\text{H}_4\text{Et})_2$ , is prepared from ethylbenzene and sulphuric anhydride. The yield is only 20 per cent., sulphonic acids also being formed. It is soluble in benzene and chloroform, and crystallises from alcohol in plates; the melting point is  $98^\circ$ , not  $102^\circ$ , as stated by Töhl and Eberhard (Abstr., 1894, i, 133). *Bi-isopropylphenylsulphone* is prepared in a similar manner, the yield being 16 per cent. It crystallises from alcohol in large prisms, and melts at  $96^\circ$ , not at  $109\text{--}110^\circ$ , as stated by Töhl and Eberhard. Attempts to prepare sulphones from metaxylene and mesitylene by this method failed.

J.N. W.

**Homologues of Ethylenediphenyldisulphone and Ethyleneditolylidisulphone: Action of Halogenalkylene compounds on Mercaptides.** By ROBERT OTTO (*J. pr. Chem.*, 1895, [2], 51, 285—315; compare Abstr., 1891, 1229).—Propylenediphenyldisulphone may be prepared in the usual manner by the action of propylene dibromide on sodium benzenesulphinate, and has previously been described by Stuffer (Abstr., 1891, 180). When heated with aqueous potash, *phenylsulphonenepropylic alcohol* is formed, together with potassium benzenesulphinate. The alcohol crystallises in small, white needles melting at  $46^\circ$ . When treated with sodium amalgam, it yields benzenesulphinic acid and normal propylic alcohol, identified by conversion into propionic acid. The *benzoate* crystallises in needles melting at  $71\text{--}72^\circ$ . On oxidation, the alcohol is not converted into the corresponding acid but is decomposed, benzenesulphonic acid being formed. The alcohol is accompanied by a substance which separates from ether in colourless crystals, melting at  $146\text{--}147^\circ$ , the constitution of which has not yet been determined.

*Propylenediparatolylidisulphone*,  $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , crystallises in small plates and melts at  $143\text{--}144^\circ$ .

*Isobutylenediphenyldisulphone* could not be obtained by the action of isobutylene bromide on sodium benzenesulphinate. Isobutylene bromide, moreover, does not react with mercaptans in the presence of sodium ethoxide to form the thio-ether, but undergoes a different reaction, in which isobutylene is produced, accompanied by the sulphide corresponding with the mercaptan employed. A small quantity of the sulphone, which melts at  $152^\circ$ , was, however, obtained when lead phenylmercaptide was used and the thio-ether oxidised.

*Pseudobutylenediphenylsulphone* may be prepared from benzenesulphinic acid. It is a thick oily mass which mixes with alcohol and ether. Aqueous soda decomposes it in the normal manner, but with difficulty. Pseudobutylene bromide reacts with the mercaptans in a similar manner to isobutylene bromide in presence of sodium ethoxide. Commercial amylene bromide reacts with sodium benzenesulphinate to form a mixture of sulphones, and with both sodium and lead phenylmercaptide to form amylene and the corresponding sulphide. It was found impossible to obtain a hexylenediphenylsulphone either by the aid of benzenesulphinic acid or of a mercaptan. With dry sodium thiophenol, or the corresponding lead compound, chloracetole yields an oily substance, which is probably the thio-ether,  $\text{CMe}_2(\text{SPh})_2$ . Propylidene chloride and sodium thiophenol yield the *thio-ether*,

$\text{CH}_2\text{Me}\cdot\text{CH}(\text{SPh})_2$ , which is an aromatic smelling oil, but has not been analysed. A. H.

**Constitution of Aromatic Sulphones.** By L. ZORN and H. BRUNEL (*Compt. rend.*, 1894, **119**, 1224—1226).—It is generally assumed that in aromatic sulphones the  $\text{SO}_2$  group is in the para-position, but neither Genvresse (*Bull. Soc. Chim.*, [3], **9**, 513) nor Töhl and Eberhard (*Abstr.*, 1894, i, 132, 133) have been able to obtain the sulphones of metaxylene and mesitylene, whilst Töhl and Eberhard have obtained diparaxylylsulphone by the action of sulphuryl chloride on paraxylene in presence of aluminium chloride.

In order to avoid the use of aluminium chloride, which often causes molecular transpositions, the authors have subjected well cooled paraxylene to the action of the vapours of sulphuric anhydride, care being taken that the temperature did not rise above  $25^\circ$ . Under these conditions diparaxylylsulphone is formed; it crystallises from alcohol in prismatic needles, melts at  $141\text{--}142^\circ$ , and is insoluble in water and soluble with difficulty in light petroleum, but dissolves in ether and benzene.

Under similar conditions, if the temperature is not allowed to rise above  $30^\circ$ , orthoxylene yields the corresponding sulphone, which crystallises from alcohol in brilliant plates melting at  $158\text{--}159^\circ$ . It is insoluble in water and soluble with difficulty in light petroleum, but soluble in ether and chloroform and very soluble in benzene.

The existence of the sulphones of ortho-xylene and paraxylene and the non-formation of sulphones from metaxylene and mesitylene shows that in aromatic sulphones the group  $\text{SO}_2$  is in the meta-position.

C. H. B.

**Action of Alkalis on Paranitrotoluenesulphonic acid.** By FRITZ BENDER (*Ber.*, 1895, **28**, 422—425; compare O. Fischer and E. Hepp, *Abstr.*, 1893, i, 697).—The substance obtained by the action of concentrated aqueous soda on paranitrotoluenesulphonic acid has hitherto been regarded as the sodium salt of dinitrosostilbenedisulphonic acid (*loc. cit.*); it consists, however, of a mixture of two compounds which the authors have identified as the salts of *dinitrodibenzylidisulphonic acid* and *azoxystilbenedisulphonic acid*; the latter dissolves in concentrated sulphuric acid with development of a red coloration; its *barium* salt is very slightly soluble. When reduced with stannous chloride and hydrochloric acid, azoxystilbenedisulphonic acid yields diamidostilbenedisulphonic acid, and oxidation with potassium dichromate and sulphuric acid converts it into dinitrostilbenedisulphonic acid.

Dinitrodibenzylidisulphonic acid is an intermediate product, the further action of alkali converting it into a stilbene derivative. The solution in concentrated sulphuric acid is orange-coloured; on reduction, it yields diamidostilbenedisulphonic acid. M. O. F.

**Action of Carbonyl Chloride on Derivatives of Sulphonic and Sulphinic acids.** By P. TISCHENDORF (*J. pr. Chem.*, 1895, [2], **51**, 350—352).—Carbonyl chloride reacts with phenylsulphone-phenylamide in the normal manner, *diphenylsulphonediphenylcarbamide*,

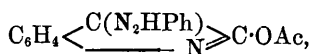
$\text{CO}(\text{NPh}\cdot\text{SO}_2\text{Ph})_2$ , which melts at  $198^\circ$ , being formed. Paratolylsulphonphenylamide reacts in a similar manner, *diparatolylsulphoneli-phenylcarbamide*, melting at  $210^\circ$ , being produced. On the other hand, phenylsulphonamide yields a substance melting at  $155^\circ$  of which the constitution has not yet been determined, and an analogous product, melting at  $180^\circ$ , is obtained from paratolylsulphonamide. These two compounds seem to be formed from three molecules of the original sulphonamide and are acids, whilst the normal derivatives are in different substances.

Sodium benzenesulphinate does not yield any analogous compound with phosgene. A. H.

### The Red Isomeride of Indigotin. Some Derivatives of Isatin.

By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1895, **28**, 539—547).—Naturally occurring indirubin, "indigopurpurin" obtained by the reduction of isatin chloride (Baeyer, *Abstr.*, 1879, 535), and synthetic indirubin obtained from isatin and indoxyl (*Abstr.*, 1882, 199), have been compared and found to be identical; the most probable formula for the substance is  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{NH}\end{smallmatrix}\rangle\text{C}:\text{C}\langle\begin{smallmatrix}\text{CO} \\ \text{C}_6\text{H}_4\end{smallmatrix}\rangle\text{NH}$ .

Isatin phenylhydrazone yields an *acetyl derivative*,



which forms yellow crystals, and melts at  $131^\circ$  when heated quickly. Isatin also yields a 1 : 4-*tolylhydrazone*, crystallising in yellow needles melting at  $233^\circ$ , and 1 : 2-*tolylhydrazone*, which forms yellow needles melting at  $240$ — $241^\circ$ ; the latter yields an *acetyl* derivative crystallising in yellow needles and melting at  $167^\circ$ . Metachlorisatin yields a 1 : 4- and a 1 : 2-*tolylhydrazone*, and a  $\beta$ -*oxime*, which crystallise in yellow needles and melt respectively at  $253^\circ$ ,  $273$ — $274^\circ$ , and  $252^\circ$ . Bromisatin yields a yellow, crystalline *phenylhydrazone*, melting at  $271$ — $272^\circ$ , the yellow *acetyl* derivative of which melts at  $224^\circ$ . Nitroisatin yields a yellow *acetyl* derivative, *acetylpsendonitroisatin*, which melts at  $193$ — $194^\circ$ , and from which, when it is dissolved in cold aqueous alkali and the solution acidified with acetic acid, the yellow *acetylnitroisatic acid*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NHAc})\cdot\text{CO}\cdot\text{COOH}$ , is obtained; this yields nitroisatin when it is boiled with acids. Nitroisatin further yields a *phenylhydrazone* and a 1 : 4- and a 1 : 2-*tolylhydrazone*; these are dark yellow, and melt at  $284^\circ$ ,  $274$ — $275^\circ$ , and above  $290^\circ$  respectively.

C. F. B.

**Metadichlor- and Metadibrom-indigo.** By ADOLF BAEYER and ERNST WIRTH (*Annalen*, 1895, **284**, 154—157; compare this vol., i, 282).—3 : 6-Bromonitrostyryl methyl ketone,



forms yellowish needles which melt at  $165.5$ — $166^\circ$ ; it is prepared by the action of boiling acetic anhydride on bromonitrophenylhydroxyethyl methyl ketone. When the latter is treated with caustic soda the

solution becomes yellow and a precipitate of metadibromindigo is formed. This colouring matter closely resembles indigo; the vapour is reddish-violet. It dissolves in hot aniline and in chloroform, but it is almost insoluble in melted paraffin. When treated with concentrated sulphuric acid, it undergoes sulphonation; dibromindigo is decolorised by alcoholic potash and undergoes oxidation with nitric acid.

Dichlorindigo resembles the dibromo-derivative; it is prepared in a similar manner from 3 : 6-chloronitrophenylhydroxyethyl methyl ketone. M. O. F.

**Conversion of Isodiazohydroxides into Derivatives of Diphenyl.** By EUGEN BAMBERGER (*Ber.*, 1895, **28**, 403—407; compare Kühling, this vol., i, 182).—By allowing paranitroisodiazobenzene hydroxide to remain in benzene, or its sodium salt in benzene and acetic acid, or its methylic salt in boiling benzene, paranitrodiphenyl is obtained;  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$ . In a similar manner, the other compounds mentioned below were prepared; the numbers given are melting points.

*Diphenyl. Parabromodiphenyl*, lustrous, white plates, with odour of oranges,  $90^\circ$ . *Paranitrodiphenyl*, very pale yellow needles,  $114\text{--}114.5^\circ$ . *Orthomethylparanitrodiphenyl*, colourless, glassy needles,  $56\text{--}57^\circ$ . *Paranitrophenyltolyl*, lustrous, white needles,  $104^\circ$ ; reduced by tin and hydrochloric acid to *paramidophenyltolyl*, the acetic derivative of which melts at  $147^\circ$ . C. F. B.

**Syntheses with Sodamide Derivatives.** By CARL BLACHER (*Ber.*, 1895, **28**, 432—437).—The sodium compound of acetamide, of benzamide, or of phenylcarbamide is obtained from a mixture of sodium ethoxide and the amide (1 mol.) in alcoholic solution on removing the solvent by distillation under reduced pressure.

Benzoylbenzylamine is formed when sodium benzamide, suspended in xylene, is heated for 13 hours with benzylic chloride in a reflux apparatus fitted with a tube of calcium chloride. Under similar conditions benzoic chloride and sodium benzamide give rise to a mixture of di- and tri-benzamide.

When a solution of iodine (1 mol.) in xylene is added to boiling xylene in which sodium benzamide is suspended, it is immediately decolorised, with formation of benzoylphenylcarbamide, which melts at  $204\text{--}205^\circ$ . If benzene or toluene is employed as the medium, an isomeric compound,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2$ , is formed; this melts at  $180\text{--}185^\circ$ .

Synthetical products were not obtained by the action of sodium benzamide on ethylic chloracetate or chloroformate, the salts undergoing decomposition prior to the formation of sodium chloride.

M. O. F.

**Action of Acid Chlorides on Methyl Paraisobutylphenyl Ether.** By FRANK B. DAINS (*Amer. Chem. J.*, 1895, **17**, 114—116).—By the action of acetic chloride, *orthomethoxymetisobutylacetophenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Bu}^s\cdot\text{COMe}$ , is formed. It is an oil which boils at  $262\text{--}265^\circ$  under 749 mm. pressure, and does not solidify at  $-18^\circ$ . With

hydroxylamine, it yields a *ketoxime* crystallising in needles melting at 113—114°.

With benzoic chloride, *orthomethoxypara-isobutylbenzophenone* is formed, boiling above 315°.

L. T. T.

**Displacement of Isodiazogroups by Cyclic Radicles.** By OTTO KÜHLING (*Ber.*, 1895, **28**, 523—527; compare this vol., i, 182).—The following compounds were prepared from anhydrous finely-divided sodium paranitrophenylnitrosamine in presence of acetic chloride or glacial acetic acid; the yield in most cases was poor. The constitution of the compounds is not definitely proved, but the substituting groups are probably in the para positions 4, 4'.

*Paranitrophenylbenzaldehyde*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ , obtained from benzaldehyde and the sodium nitrosamine, crystallises in minute plates, melts at 115—120°, and yields a crystalline *hydrogen sodium sulphite* derivative. *Paranitrophenylacetophenone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{Me}$ , formed from the nitrosamine and acetophenone, crystallises in slender, pale yellow needles, and melts at 90—94°. No oxime could be obtained. *Paranitrophenylbenzoic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , is prepared from ethylic benzoate and the nitrosamine, the resulting uncrystallisable *ethylic salt* being hydrolysed with alcoholic potash; it is a crystalline, yellowish powder, melts at 189°, and when slowly heated evolves carbonic anhydride at 100°. It dissolves in alkalis and alkali carbonates with a yellow colour. *Paranitrohydroxydiphenyl*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is obtained from ethoxybenzene and the nitrosamine; the *ethylic salt* which is first formed does not crystallise; the phenol is deposited in slender, yellow needles, melts at 120°, and gives a reddish-brown coloration with ferric chloride. Schmidt and Schultz give the melting point of 4 : 4'-nitrohydroxydiphenyl as 170°. *Paranitrophenylbenzylic alcohol*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$ , formed from benzylic alcohol and the nitrosamine, crystallises in slender, colourless, concentrically-grouped needles, and melts at 121—122°.

*Paranitrophenylpyridine*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_5\text{NH}_4$ , prepared from pyridine and the nitrosamine, crystallises in aggregates of small yellow needles, and melts at 117°, with previous softening at 109°. It is a feeble base, and dissolves in dilute acids; the *hydrochloride* is unstable, the *sulphate* stable. In reply to Bamberger's criticism (*Ber.*, **28**, 403) of his previous paper (*loc. cit.*), the author repeats his conviction that the sodium salt acts in the tautomeric form,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{NONa}$ , and that acidyl derivatives are produced by its interaction with acid chlorides in presence of anhydrous benzene. Support for this view is found in the readiness with which the nitrogen is eliminated.

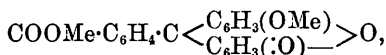
J. B. T.

**Diphenylorthophthalide.** By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 513—514).—*Diphenylorthophthalide*,  $\text{CO} < \text{C}_6\text{H}_4 > \text{C}(\text{C}_{12}\text{H}_9)_2$ , is prepared by Friedel-Craft's method from diphenyl and phthalic chloride; it is purified with difficulty, crystallises from acetic acid in granules or small plates, softens at 98—100°, and is not completely melted at 120°. When warmed with concentrated sulphuric acid, a cherry-red coloration is formed, which slowly changes to dull green;

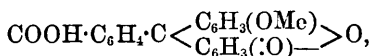


at ordinary temperatures, the colour produced is deep blue, changing somewhat quickly to violet. The yield is 30 per cent. of the theoretical. Variation in the proportion of diphenyl employed is without effect on the composition of the resulting product. J. B. T.

**Fluoresceïn Ethers.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1895, **28**, 396—399; compare Nietzki and Schröter, this vol., i, 183).—When fluoresceïn is boiled with caustic potash and methylic iodide in methyl alcoholic solution, it yields a *dimethyl compound*,



which forms orange, or deep red, metallic crystals, melts at 208°, and gives a green fluorescence in alcoholic solution; none of the colourless isomeride, which melts at 198° (this vol., i, 55), is formed. This dimethyl compound is converted by dilute sodium hydroxide into a nearly colourless *monomethyl ether*,



which melts at 262°, gives a yellow coloration with green fluorescence in alkaline solution, and, when boiled with aniline and aniline hydrochloride, yields an *anilide*,  $\text{NPh} \cdot \text{C} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{O} \end{matrix} > \text{C} < \begin{matrix} \text{C}_6\text{H}_3 \cdot \text{OMe} \\ \text{C}_6\text{H}_3 \cdot \text{OH} \end{matrix}$ , which forms colourless crystals, and gives no colour or fluorescence in alkaline solution, although in strong sulphuric or hydrochloric acid solution it is yellow with green fluorescence. The property of fluorescence in alkaline solution seems to depend, in the case of the anilides, on one particular hydroxyl group remaining intact, namely, that which is still present in the compounds with a quinonoid formula, and which in the anilide of the monomethyl ether is replaced by methoxyl. C. F. B.

**Constitution of Fluoresceïn.** By RICHARD MEYER (*Ber.*, 1895, **28**, 428—432; compare Abstr., 1892, 1228).—When fluoran is gently heated with fused caustic alkali, a mixture of benzoic and salicylic acids with orthodihydrobenzophenone and phenol is formed.

The salts of hydrofluoranic acid (*loc. cit.*) are characterised by a low degree of solubility; the *sodium* salt forms colourless plates which resemble naphthalene. The *barium* and *magnesium* salts form minute crystals, whilst the *strontium*, *zinc*, *copper*, and *silver* salts are amorphous. The *methylic* salt crystallises in long needles, and melts at 123—125°; the *ethylic* salt separates from alcohol in plates and melts at 99—101°. M. O. F.

**Oxidation of Naphthalene Tetrachloride.** By D. HELBIG (*Ber.*, 1895, **28**, 505—507).—Naphthalene tetrachloride,  $\text{C}_{10}\text{H}_6\text{Cl}_4$  [ $\text{Cl}_4 = 1 : 2 : 3 : 4$ ], when oxidised with nitric acid (sp. gr. 1.45), yields dichloronaphthoquinone [ $\text{CO} = 1 : 4$ ;  $\text{Cl}_2 = 2 : 3$ ] which melts at 196°, not 189° as stated by Graebe. With chromic anhydride in glacial acetic acid solution, naphthalene tetrachloride gives 3 : 4-

dichloro-1-naphthol; when this is exposed to the air in alkaline solution, a deep blue compound is formed which is being further investigated. The oxidation of naphthalene tetrachloride with potassium permanganate has not led to any definite results. J. B. T.

**New Formation of Secondary Amines.** By OTTO KYM (*J. pr. Chem.*, 1895, [2], 51, 325—335).— $\alpha$ -Bromonaphthalene reacts with aniline and paratoluidine in the presence of soda-lime in the same way as bromobenzene (Merz and Paschkowesky, *Abstr.*, 1894, i, 122). The product, however, consists not of the corresponding derivative of  $\alpha$ -naphthylamine, but the isomeric  $\beta$ -compound. Molecular change, therefore, takes place in this reaction, and the same thing is observed when  $\alpha$ -chloronaphthalene is heated with paratoluidine and soda-lime, paratolyl- $\beta$ -naphthylamine being formed. A somewhat similar change occurs when paradibromobenzene is heated with paratoluidine and soda-lime, diparatolylmetaphenylenediamine being produced, and not the expected derivative of paraphenylenediamine. A. H.

**Chrysophanic acid.** By OSWALD HESSE (*Annalen*, 1895, 284, 191—195).—Chrysophanic acid has been the subject of much investigation. It is isolated from the root of the rhubarb plant by extracting it several times with ether; the accumulated extracts, with exception of the first, are evaporated, and the residue is treated with a small quantity of alcohol, filtered, and dissolved in chloroform. On removing the solvent by evaporation and treating the residue with warm aqueous potassium carbonate, the substance remains undissolved. Chrysophanic acid crystallises from alcohol in small leaflets and melts at  $178^{\circ}$ ; the analysis of the compound agrees with the formula  $C_{15}H_{10}O_4$ . Hydriodic acid converts it into chrysophanohydroanthrone,  $C_{15}H_{12}O_3$ , which melts at  $196^{\circ}$  (*Abstr.*, 1888, 492).

M. O. F.

**Picene.** By EUGEN BAMBERGER and FREDERICK D. CHATTAWAY (*Annalen*, 1895, 284, 52—80; compare *Abstr.*, 1893, i, 594).—On distilling picenequinone with zinc dust, picene is obtained in nacreous plates which exhibit a blue fluorescence. When the vapour of the hydrocarbon is led through a red-hot tube containing hydrogen, hydro-picene,  $C_{22}H_{18}$ , is formed; it is also obtained by the action of heated litharge on picenequinone. Hydro-picene forms small needles and melts at  $285^{\circ}$ ; distillation with zinc dust converts it into picene.

*Picenequinone* or *picylenediketone*,  $\begin{matrix} C_{10}H_6 \cdot CO \\ | \\ C_{10}H_6 \cdot CO \end{matrix}$ , is produced when picene, suspended in boiling glacial acetic acid, is treated with a solution of chromic anhydride in the same solvent; a small quantity of picenequinonecarboxylic acid is formed at the same time. The quinone is a brick-red, crystalline powder which yields lustrous, red leaflets and needles on sublimation; when distilled with soda lime, it gives rise to  $\beta\beta$ -dinaphthyl and picene.

*Picylene ketone*,  $C_{20}H_{12} \cdot CO$ , may be prepared in several ways. It is formed when a mixture of picenequinone or picenequinonecarboxylic acid and litharge is distilled in a vacuum; the ketone is obtained by distilling picenic acid from lime, and by heating the silver salt at

150—200°; it is also prepared from picenic acid by the action of cold concentrated sulphuric acid. Picylene ketone is a golden-yellow powder which melts at 185·5°; it dissolves in concentrated sulphuric acid with development of a violet coloration, and is precipitated from the solution on the addition of water.

*Picylencarbinol*, or *picenefluorene alcohol*,  $\begin{matrix} \text{C}_{10}\text{H}_6 \\ | \\ \text{C}_{10}\text{H}_6 \end{matrix} > \text{CH}\cdot\text{OH}$ , is prepared by reducing the foregoing ketone with zinc dust and hydrochloric acid; sodium amalgam may also be employed as the reducing agent. It melts at 230° and dissolves in warm concentrated sulphuric acid with development of a blue coloration. The *acetyl*-derivative crystallises in slender, white needles and melts at 159°.

*Piculenemethane*, or *picenefluorene*,  $\begin{matrix} \text{C}_{10}\text{H}_6 \\ | \\ \text{C}_{10}\text{H}_6 \end{matrix} > \text{CH}_2$ , is formed when picylene ketone is heated with hydriodic acid and phosphorus for four hours at 170—175°; it melts at 306°, and the solution in concentrated sulphuric acid is green.

Picenic ( $\beta\beta$ -dinaphthylcarboxylic) acid,  $\text{C}_{10}\text{H}_7\cdot\text{C}_{10}\text{H}_6\cdot\text{COOH}$ , is prepared by acting on picylene ketone with fused potash. Picenequinone also yields the acid under this treatment, but in much smaller quantity, picylene ketone, picene, hydropicene, and dinaphthyl being formed at the same time. Picenic acid melts at 201°; the *barium*, *calcium*, and *silver* salts are colourless, and are not readily soluble in water.

It has already been stated (*loc. cit.*) that picenic acid when distilled from lime in a vacuum yields  $\beta\beta$ -dinaphthyl. If the operation is carried out under atmospheric pressure, a *hydrocarbon*, which melts at 235°, is formed; it crystallises from alcohol in white, nacreous plates.

*Picenequinonecarboxylic acid*,  $\begin{matrix} \text{COOH}\cdot\text{C}_{10}\text{H}_5\cdot\text{CO} \\ | \\ \text{C}_{10}\text{H}_5\cdot\text{CO} \end{matrix}$ , is obtained by the oxidation of picene with potassium dichromate and sulphuric acid; it is a red, crystalline powder which becomes black at 250° and decomposes at about 330°. The solution in concentrated sulphuric acid is dark violet, whilst alkalis and alkali carbonates dissolve it with development of a deep red coloration. The *silver* salt is a dark red powder; when heated in small quantities at 180—200°, it yields a sublimate of picenequinone. On distilling picenequinonecarboxylic acid from lime, picene is produced, and the hydrocarbon is also formed, together with hydropicene and picylene ketone, when picenequinonecarboxylic acid is distilled from litharge in a vacuum. In preparing picenequinonecarboxylic acid by oxidation of picene, phthalic acid is formed in small quantity; this substance is also produced on oxidising picenequinonecarboxylic acid with potassium permanganate.

*Picencarboxylic acid*,  $\begin{matrix} \text{COOH}\cdot\text{C}_{10}\text{H}_5\cdot\text{CH} \\ | \\ \text{C}_{10}\text{H}_5\cdot\text{CH} \end{matrix}$ , is prepared by heating picenequinonecarboxylic acid with hydriodic acid and phosphorus for eight hours at 170—180°; it is a white powder which melts at 245°. The *silver*, *barium*, and *calcium* salts do not dissolve in water. When the acid is distilled from lime in a vacuum, picene is formed.

M. O. F.

**Pine Tar.** By ADOLPHE RENARD (*Compt. rend.*, 1894, **119**, 1276—1277).—The products of the distillation of pine tar boiling above  $300^{\circ}$  consist of a mixture of diterebenthyl,  $C_{20}H_{30}$ , boiling at  $332$ — $338^{\circ}$ , and diterebenthylene,  $C_{20}H_{28}$ , boiling at  $340$ — $345^{\circ}$ , identical with those found in resin oils, except that in the latter the diterebenthyl is present in much higher proportion. The two are readily separated by the action of sulphuric acid, which converts diterebenthyl into a sulphonic derivative, but has no action on diterebenthylene. Didecene, which is found in resin oils, is not present in the products of the distillation of pine tar. The final fractions contain retene, which is readily purified by pressure and crystallisation from alcohol.

The phenols obtained by the action of sodium hydroxide on the crude product of distillation of the tar, boil almost entirely between  $190^{\circ}$  and  $230^{\circ}$ , 66 per cent. boiling between  $200^{\circ}$  and  $220^{\circ}$ . The fraction  $200$ — $210^{\circ}$ , when analysed by Béhal and Choay's method, was found to consist of monhydric phenols, 40.0 per cent.; guaiacol, 20.3 per cent.; creosol and its homologues, 37.5 per cent. The fraction  $210$ — $220^{\circ}$  contained no guaiacol. So far as regards the proportion of guaiacol, pine-tar creosote is intermediate between that from the beech and that from the oak (compare Abstr., 1894, i, 612).

C. H. B.

**Rotatory Power of Oil of Spike and Oil of Lavender.** By GUSTAVE MASSOL (*J. Pharm.*, 1895, [6], **1**, 49—50).—The author has determined the rotation of samples of known origin and purity. He found for oil of lavender,  $[\alpha]_D = -3.70^{\circ}$ , and sp. gr. = 0.930 at  $15^{\circ}$ ; and for oil of spike,  $[\alpha]_D = +9.66^{\circ}$ , and sp. gr. = 0.935 at  $15^{\circ}$ . Buignet found, for lavender,  $[\alpha]_D = -21.20^{\circ}$ , and sp. gr. = 0.886; for spike,  $[\alpha]_D = +3.30^{\circ}$ , sp. gr. = 0.886; and Bruylants, for lavender,  $[\alpha] = -4.01^{\circ}$ , and sp. gr. = 0.876; and spike,  $[\alpha] = -0.64^{\circ}$ , and sp. gr. = 0.908. It is thus clear that the rotatory power and density of these oils are dependent on the character of the season, soil, &c., and cannot be used as tests of purity.

L. T. T.

**Essence of Ylang-ylang.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1894, [3], **11**, 577—583).—The sesquiterpene mentioned in the previous paper (this vol., i, 243) consisted mainly of a fraction boiling at  $138.5$ — $143^{\circ}$ . The sp. gr. = 0.91 at  $15^{\circ}$ , the refractive index = 1.50001 at  $20^{\circ}$ , the rotatory power of the liquid =  $+46.4^{\circ}$  for 20 mm.; of the alcoholic solution (about 9 per cent.),  $[\alpha]_D = +6.8^{\circ}$ . The molecular refraction is 66.32, a number pointing to the presence of two ethylene bands in the molecule. The hydrochloride,  $C_{15}H_{24} \cdot 2HCl$ , crystallises from ethylic acetate in brilliant needles and melts at  $117^{\circ}$ . A small quantity of a solid polyterpene was also isolated.

On repeating the work on a fresh portion of essence, a considerable quantity of acetic acid was found in alcoholic combination. The constants of the ylangol obtained were as follows, at  $17^{\circ}$ :—sp. gr. = 0.8907; refractive index = 1.4747; molecular refraction = 48.64; specific rotatory power in alcoholic solution,  $[\alpha]_D = -19.3^{\circ}$ . A small quantity of the sodium hydrogen sulphite compound of the oxidation product of the ylangol was isolated.

The proximate percentage composition of essence of ylang-ylang is

thus:—benzoic acid, 9; acetic acid, 7; ylangol, 30—32; sesquiterpene, 30; polyterpenes and volatile products, 20. JN. W.

**Metallic Campholates.** By GUERBET (*Bull. Soc. Chim.*, 1894, [3], 11, 486—491).—A revision and completion of Kachler's and Malin's work (*Annalen*, 1872, 162, 259, and 1868, 145, 201).

*Ammonium campholate*,  $C_{10}H_{17}O_2NH_4$ , is prepared by the action of dry ammonia on an ethereal solution of campholic acid; it is very unstable, and dissociates rapidly in air, and at once in water, so that Kachler's statement that it can be obtained by evaporating an ammoniacal solution of the acid is not correct; the acid itself remains. The *potassium*, with  $2H_2O$ ; *sodium*, with  $5H_2O$ ; *barium*, with  $3H_2O$ ; *strontium*, *calcium*, *magnesium*, *zinc*, *copper*, *nickel*, and *cobalt* salts were prepared and analysed. JN. W.

**Alkylic Campholates.** By GUERBET (*Bull. Soc. Chim.*, 1894, [3], 11, 491—496).—The alkylic campholates can be prepared by the action of campholic chloride on the respective alcohols. The yield obtained by the action of the free acid on the alcohols is very poor; the rate of formation of the isobutylic salt, for instance, is never greater than 0.1, and the limit of etherification at  $155-170^\circ$  is 27.1 per cent. The acid properties of campholic acid are thus extremely feeble, and the alkylic salts resemble ethers rather than ethereal salts; they are not hydrolysed by aqueous or alcoholic alkalis under ordinary conditions, but are readily decomposed by hydrogen chloride or iodide; they are completely hydrolysed, however, by alcoholic sodium ethoxide at  $150^\circ$ .

The alkylic campholates are colourless, oily liquids of agreeable odour. *Methylic campholate*,  $C_{10}H_{17}O_2Me$ , boils at  $208^\circ$ , and has sp. gr. = 0.9723 at  $0^\circ$ . The *ethylic* salt boils at  $220^\circ$  (750 mm.) and at  $106-107^\circ$  (20 mm.), and has sp. gr. = 0.9534 at  $0^\circ$ ; it does not solidify at  $-20^\circ$ ; the odour resembles that of peppermint. The *isopropylic* salt boils at  $228^\circ$ , and has sp. gr. = 0.9377 at  $0^\circ$ . The *isobutylic* salt boils at  $250^\circ$ , and has sp. gr. = 0.9365 at  $0^\circ$ . The *amylic* salt boils at  $263-265^\circ$ , and has sp. gr. = 0.9361. The *phenylic* salt melts at  $22^\circ$  and boils at  $305^\circ$ ; the odour recalls that of phenol. JN. W.

**Camphoric acid.** By WILLIAM A. NOYES (*Ber.*, 1895, 28, 547—555).—A preliminary notice; the full account will appear in the *Amer. Chem. J.*—Dihydroamidocampholytic acid (Abstr., 1894, i, 339), when treated with nitrous acid, yields *dihydrohydroxycampholytic acid*,  $OH \cdot C_8H_{14} \cdot COOH$ , melting at  $132^\circ$ ; this is probably a  $\beta$ -hydroxy-compound, and, if so, camphoric acid has its two carboxyl groups attached to neighbouring carbon atoms.

Liquid (cistrans) campholytic acid, when warmed with dilute sulphuric acid, is transformed into an isomeric *iso-* or *cis-campholytic acid*, melting at  $133.5^\circ$ , identical with the camphothetic acid of Walker (*Trans.*, 1893, 504) and the isolauronic acid of Königs and Hoerlin (Abstr., 1893, i, 363); the author regards the two acids as stereoisomeric, containing respectively, in the group  $-CMe:C(COOH)-$ ,

the Me and COOH on opposite and on the same side of the plane of the ring. The cistrans acid yields a *hydrobromide* melting at 98—100°, and a *dibromide* melting at 114°; the cis-acid, although with difficulty, a *hydrobromide* melting at 127—130°, and a *dibromide* melting at 138—140°.

Amidolauronic acid was treated with nitrous acid, and the following products were isolated. (1) A *hydrocarbon*,  $C_8H_{14}$ , boiling at 122°, and with sp. gr. = 0.8033 at 15°/15°, = 0.8004 at 20°/20°, probably identical with the one obtained by Aschan (this vol., i, 154). (2) Unsaturated ( $\beta\gamma$ ) *isolauronic acid*,  $C_8H_{13}\cdot COOH$ ; its *calcium salt* crystallises with  $2H_2O$ ; the *amide* is liquid; heating with dilute sulphuric acid converts the acid into campholactone. (3) *Isocampholactone*, melting at 23°, probably stereoisomeric with campholactone. (4) An acid melting at 180°, perhaps



C. F. B.

**Camphoric Dianilide.** By OSSIAN ASCHAN (*Ber.*, 1895, 28, 530—531).—Camphoric chloride is mixed with rather more than 2 mols. of aniline, both substances being dissolved in ether and the mixture kept cool; aniline hydrochloride is then removed by shaking with water, and the ethereal solution allowed to remain; crystals of the *dianilide*,  $C_6H_5(CO\cdot NHPH)_2$ , are deposited. The dianilides from *d*- and *l*-camphoric acid are entirely similar in properties, and melt at 226°; those of the optically isomeric isocamphoric acids also resemble each other, but they melt at 201°, and are much more soluble in alcohol and acetic acid than the two first mentioned. C. F. B.

**Chlorophyll.** By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Annalen*, 1895, 284, 81—107; compare Abstr., 1893, i, 41, and 1894, i, 341).—Alkachlorophyll is prepared by a method differing only in minor particulars from the process already described (*loc. cit.*). The product undergoes no apparent change on dissolution in hydrochloric acid, and the colour of the liquid remains unaltered for many days; on pouring the solution into water, however, ether extracts phyllotaonin, and ethylphyllotaonin is formed when the solution in hydrochloric acid is poured into boiling alcohol, a purple-blue coloration being developed. Concordant analyses of alkachlorophyll agree equally well with the formulæ  $C_{30}H_{34}N_4O_4$  and  $C_{32}H_{37}N_7O_7$ , but its behaviour, when treated with hydrochloric acid, points to the latter expression as representing the composition, because phyllotaonin has already been shown to have the formula  $C_{40}H_{40}N_6O_6$ .

Alkachlorophyll is a dark, greenish-blue substance, which dissolves readily in alkalis, forming dark, emerald-green solutions, exhibiting a strong, red fluorescence. The sodium salt resembles it in appearance, and the absorption spectrum of the aqueous solution differs but slightly from that of the colouring matter itself. When alkachlorophyll is heated for several hours at 190—200° with alcoholic potash, brownish-red crystals are obtained, which dissolve in hydrochloric acid, forming a reddish-violet solution; on neutralising the filtered liquid with soda and acidifying with acetic acid, ether extracts a

substance which the authors term *phylloporphyrin*; it is not identical with the compound to which this name has been applied by Hoppe-Seyler, who obtained it from dichromatic acid by the action of acids. The spectrum of an ethereal solution of alkachlorophyll shows, in addition to the four absorption bands of chlorophyll, a fifth band at F, but this does not appear when hydrochloric acid is the solvent employed.

Phylloporphyrin is prepared by heating phyllotaonin for several hours at  $190^{\circ}$  with alcoholic potash; on diluting the liquid and acidifying with hydrochloric acid, ether extracts a brown substance. This is boiled with alcohol, filtered, and the filtrate treated with an alcoholic solution of zinc acetate. The red, crystalline substance slowly deposited from this solution is a zinc salt, which is decomposed by adding hydrochloric acid to the hot alcoholic solution, this being then poured into a large quantity of water and extracted with ether. Evaporation of the solvent yields phylloporphyrin, which, on recrystallisation from alcohol, is obtained in short, reddish-violet prisms. Analysis gives results which agree with the formula  $C_{32}H_{34}N_4O_2$ . Phylloporphyrin is easily soluble in chloroform, but dissolves with difficulty in alcohol, ether, and carbon bisulphide, giving red solutions, which exhibit fluorescence of the same colour; this acquires a bluish tint on the addition of acids. Phylloporphyrin has basic properties, but it also forms metallic salts. The spectrum of an ethereal solution has seven absorption bands; a plate representing the spectra of solutions in sulphuric and hydrochloric acids and in ether, together with the aqueous solution of the zinc salt, appears in the original paper, which also contains a detailed description of the method by which the authors have succeeded in converting phylloxanthin into phyllocyanin.

M. O. F.

**Compounds from Lichens.** By WILHELM ZOPF (*Annalen*, 1895, 284, 107—132).—*Pinastric acid*,  $C_{10}H_8O_3$ , is the pigment to which *Cetraria pinastri* (Scopoli) owes its yellow colour; the air-dried lichen is extracted with ether, and the residue obtained on evaporating the solvent is recrystallised several times from absolute alcohol in order to remove the usnic acid which is present. Pinastric acid crystallises from alcohol in golden-yellow prisms, and melts at  $203$ — $205^{\circ}$ . Alkalis and alkali carbonates dissolve it, forming yellow solutions which are decomposed by carbonic anhydride; the solution in concentrated sulphuric acid is yellow. When heated for an hour with acetic anhydride, pinastric acid is converted into a compound,  $C_{18}H_{16}O_6$ , crystallising from alcohol in lustrous, greenish needles which melt at  $171$ — $173^{\circ}$ . Pinastric acid has toxic properties; it occurs in several other yellow lichens.

*Soloric acid*,  $C_{18}H_{14}O_6$ , is the substance giving rise to the red colour which characterises the under surface of the thallus of *Solorina crocea* (L.). On extracting the lichen with chloroform, and evaporating the dark, reddish-brown liquid, a crystalline mass is obtained which, after being recrystallised several times from benzene and a mixture of benzene and alcohol, yields small, red, lustrous crystals which melt at  $199$ — $201^{\circ}$ ; these crystals are pleochroic. Reddish-

yellow or reddish-brown solutions are formed by dissolving soloric acid in chloroform, benzene, light petroleum, ether, and alcohol; it is insoluble in water. Soda and potash form violet solutions, whilst, if warmed with ammonia or alkali carbonates, it gives purple-violet solutions which are decomposed by carbonic anhydride. Crystals of the acid, when treated with boiling aqueous barium hydroxide, become dark violet, but remain undissolved; it is insoluble in nitric acid, and dissolves without change in concentrated sulphuric acid, being reprecipitated from the purple solution on diluting it with water. Boiling acetic anhydride converts soloric acid into a *diacetyl* derivative which crystallises in small, golden-yellow needles, and melts at 147—148°.

*Rhizocarpic acid*,  $C_{13}H_{10}O_3$ , is obtained from *Rhizocarpon geographicum* (L.) and *R. lecanorinum* by extraction with chloroform and recrystallisation of the product from absolute alcohol; it crystallises in lemon-yellow, rhombic prisms, and melts at 177—179°. Alkalis and alkali carbonates dissolve the acid forming yellow or yellowish-green solutions which are not decomposed by carbonic anhydride; it is soluble in concentrated sulphuric and nitric acids. When treated with boiling acetic anhydride, rhizocarpic acid is converted into ethylpulpic acid which melts at 128°. Rhizocarpic acid also occurs in *Pleopsidium chlorophanum* (Wahlenberg), *Raphiospora flavovirescens* (Borr.), and *Biatora lucida* (Ach.). From the first-named of these, a compound was also obtained which melts at 144—145°; it crystallises in colourless, silvery leaflets belonging to the tetragonal system, and, from its source, the author terms it *pleopsidic acid*.

Methylic hydrogen pulvate or vulpic acid (J. Volhard, this vol., i, 99) occurs in the lichens *Calycium chlorinum* (Korber), *C. c.* (Stenh.), and *Cyphelium chrysocephalum* (Ach.), whilst *Callopusma vitellinum* (Ehrhardt), and *Physcia medians* (Nylander) contain the ethylic salt.

Calycin (Hesse, Abstr., 1881, 180) is present in the lichens *Lepra candelaris* (Schaerer), *L. chlorina* (Ach.), *Calycium Stenhammari*, *Callopusma vitellinum* (Ehrhardt), *Gyalolechia aurella* (Hoffm.), *Physcia medians* (Nylander), and *Candelaria concolor* (Dicks). On agitating a solution of calycin in chloroform or benzene with aqueous soda or potash, a brick-red substance is produced; this is taken up by the alkali, leaving the organic solvent colourless. The lichen from which calycin was first isolated is *Lepra candelaris* (compare *loc. cit.*); vulpic acid occurs in *Calycium* (*cyphelium*) *chrysocephalum*; but this lichen does not contain calycin.

Psoromic acid (Spica, Abstr., 1883, 80) occurs in *Rhizocarpon geographicum* (L.), together with rhizocarpic acid. The author has obtained zeorin from *Physcia caesia* (Hoffmann), and *P. endococcina*.

M. O. F.

**Compounds from Lichens.** By OSWALD HESSE (*Annalen*, 1895, 284, 157—191).—Usnic acid,  $C_{16}H_{16}O_7$ , is obtained from *Usnea barbata* var. *ceratina*; it melts at 195—196°. An intense brownish-red coloration is developed in the alcoholic solution by ferric chloride. When heated with acetic anhydride at 85°, the *anhydride*,  $C_{36}H_{30}O_{13}$ , is formed; it crystallises in lustrous, yellow needles, and melts at 189°. The potassium salt contains  $3H_2O$ , the sodium and lead salts,



$2\text{H}_2\text{O}$ , and the barium and calcium salts,  $4\text{H}_2\text{O}$ ; the copper and silver salts are anhydrous. When usnic acid is heated at  $120^\circ$  with phenylhydrazine, a *dihydrazone*,  $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_6$ , is formed. It separates from alcohol in large crystals containing  $3\text{H}_2\text{O}$ , and melts at  $229^\circ$ .

On heating usnic acid for four hours with alcohol at  $150^\circ$ , decarbusnein,  $\text{C}_{17}\text{H}_{18}\text{O}_6$ , is formed (compare Paternò, Abstr., 1882, 1080). It crystallises in small, white needles, and melts at  $175^\circ$ ; treatment of the alcoholic solution with ferric chloride gives rise to a reddish-brown coloration. The acetyl derivative is obtained by the action of acetic anhydride at  $85^\circ$  (compare *loc. cit.*); it melts at  $112^\circ$ , and the alcoholic solution gives a violet coloration with ferric chloride. The action of 50 per cent. potash at  $100^\circ$  converts usnic acid into resinous products together with acetone and carbonic anhydride. When treated with concentrated sulphuric acid, usnic acid yields the isomeric usnolic acid (Stenhouse and Groves, Trans., 1881, 235); this melts at  $206\text{--}208^\circ$ , gas being evolved at  $210^\circ$ .

*Barbatin*,  $\text{C}_9\text{H}_{14}\text{O}$ , is obtained from the same source as usnic acid. It crystallises from glacial acetic acid in colourless needles, and melts at  $209^\circ$ ; it may be distilled without undergoing change. Carbon-usnic acid occurs in the lichens *Usnea barbata* var. *florida* and *hirta*. *Parmelia perlata* contains vulpic and usnic acids; a compound,  $\text{C}_{16}\text{H}_{16}\text{O}_7$ , which the author terms *parmelin*, is also present; it melts at  $187^\circ$ , and is soluble in aqueous alkalis.

*Coccellic acid*,  $\text{C}_{20}\text{H}_{22}\text{O}_7$ , is obtained from *Cladonia coccifera*; it crystallises from glacial acetic acid in colourless prisms, and melts and evolves gas at  $178^\circ$ , forming a white sublimate. Ferric chloride colours the alcoholic solution bluish-violet, whilst calcium hypochlorite develops an intense yellow colour which is destroyed on further addition of the reagent. When coccellic acid is boiled with aqueous strontium hydroxide, carbonic anhydride is eliminated with formation of *mesorcinol*,  $\text{C}_9\text{H}_{12}\text{O}_2$ .

From *Cetraria juniperina* var. *pinastri* or *Evernia pinastri* (? *prunastri*) the author has isolated a compound which he terms *chrysocetraric acid*; it melts at  $178^\circ$ , and the analysis agrees with the formula  $\text{C}_{19}\text{H}_{14}\text{O}_6$ , but in other respects it closely resembles pinastric acid described by Zopf (preceding abstract), who obtained it from *Cetraria pinastri* and *C. juniperina*.

On extracting *Parmelia parietina* (Ach.) or *Physcia parietina* (Schaer) with ether, a compound is obtained which the author proposes to call *physcion*, this name being selected in preference to chrysophyscin (Abstr., 1894, i, 541) and fiscic acid (Abstr., 1882, 1083), owing to its quinonic character and to the fact that the colour is brick-red instead of golden. *Physcion*,  $\text{C}_{16}\text{H}_{12}\text{O}_5$ , melts at  $207^\circ$ ; the alcoholic solution is neutral. With alcoholic potash it forms a bluish-violet, amorphous compound,  $\text{C}_{16}\text{H}_{12}\text{O}_5 \cdot 2\text{KOH}$ , which yields the compound  $\text{C}_{16}\text{H}_{12}\text{O}_5 \cdot \text{KOH}$  on treatment with water; this crystallises in purple needles, and both substances are decomposed by water and carbonic anhydride. *Physcion* does not combine with hydroxylamine, but it forms a crystalline compound with phenylhydrazine. The *diacetyl* derivative crystallises in greenish-yellow needles, and melts at  $183^\circ$ ; the *benzoyl* and *dibenzoyl* derivatives melt at  $171^\circ$  and

230° respectively. The *mononitro*-derivative crystallises from glacial acetic acid in small orange needles, and melts at 210°; the solution in ammonia is red, and the *sodium* salt forms cherry-red needles. The *dinitro*-derivative melts at 96°, and gives rise to highly-coloured salts.

*Protophyscion*,  $C_{15}H_{10}O_5$ , is obtained by heating physcion with hydriodic acid; it forms lustrous, brown needles, and melts at 198°.

*Physconic acid*,  $C_{16}H_8O_6$ , is formed when physcion is fused with potash; it is a bluish-black powder which decomposes without previous fusion. It resists the action of hydriodic acid and of acetic anhydride.

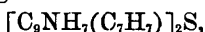
On adding zinc dust to a solution of physcion in glacial acetic acid, a compound,  $C_{16}H_{14}O_5$ , is formed which the author terms *physcihydrone*; it crystallises in pale, yellow needles, and melts at 180—182°. Fuming hydriodic acid converts it into *protophyscihydrone*,  $C_{15}H_{12}O_5$ , which melts at 210°.

In addition to physcion, the lichen from which it is derived contains physcianin and physciol. *Physcianin*,  $C_{10}H_{12}O_4$ , forms colourless prisms, and melts at 143°; at high temperatures it sublimes. An alcoholic solution is coloured bluish-violet by ferric chloride, whilst calcium hypochlorite develops a blood-red coloration which disappears when more of the reagent is added. *Physciol*,  $C_7H_5O_3$ , crystallises in slender, colourless needles; it melts at 107°, and volatilises at higher temperatures. An alcoholic solution becomes greenish-black on addition of ferric chloride, whilst calcium hypochlorite produces a yellowish-brown coloration.

M. O. F.

### Sulphides and Hydrosulphides of Aromatic Bases.

By ALBERT EDINGER (*J. pr. Chem.*, 1895, [2], 51, 91—96).—When quinoline benzyl chloride is treated with sodium hydrosulphide in concentrated aqueous solution, a white precipitate is produced which rapidly decomposes in the air. It has the formula  $C_9NH_7(C_7H_7)SH$ , and when rapidly dissolved in ether and treated with alcoholic platinic chloride in a freezing mixture yields a substance,  $(C_{16}H_{15}NS)_2PtCl_4$ , as a pale yellow precipitate, decomposing at 223°. Quinoline benzyl chloride reacts with potassium sulphide in a similar manner, yielding a substance of the formula



which also reacts with platinic chloride, forming a brown substance of the formula  $S(C_{16}H_{14}N)_2PtCl_4$ , which decomposes at 228°. When boiled with alcohol, both of these bases are converted into the same red, amorphous, comparatively stable substance which has the composition  $C_{16}H_{15}NS$ , but is not identical with the compound described above. When the quinoline benzyl chloride is treated with potassium mercaptide, a light, yellow, unstable oil is obtained which yields a platinum compound,  $[C_9H_7N(C_7H_7)SEt]_2PtCl_4$ , melting at 219°.

A. H.

**Iodisoquinoline.** By ALBERT EDINGER (*J. pr. Chem.*, 1895, [2], 51, 204—210).—*Isoquinoline tetriodide* is prepared by dissolving iodine (4 atoms) in carbon bisulphide and adding the solution to one

of isoquinoline (1 mol.) in the same solvent; after a time, dark blue crystals melting at  $130^{\circ}$  separate. It is freely soluble in alcohol and acetone, but only very sparingly in chloroform, ether, or carbon bisulphide; it loses iodine when exposed to air.

*Iodoisoquinoline diiodide*,  $C_9H_6I_2N$ , is obtained by heating isoquinoline (10 grams) with iodine (20 grams), iodic acid (5 grams), and water (200 c.c.) in a reflux apparatus for  $1\frac{1}{2}$  hours. The oily product crystallises from alcohol, and melts at  $101^{\circ}$ . When its aqueous solution is treated with sulphurous acid, it yields *iodisoquinoline hydriodide*, which crystallises in light brown needles, and melts at  $173^{\circ}$ . From this, *iodisoquinoline* is obtained by treatment with caustic soda; it crystallises in white needles, melts at  $99^{\circ}$ , and is sparingly soluble in water, but freely in organic solvents; it sublimes and distils, resembling aromatic amines in all the usual reactions. The *methiodide* (m. p.  $258-259^{\circ}$ ), *platinochloride*, with  $2H_2O$ , *picrate* (m. p.  $206^{\circ}$ ), and *chromate* (m. p.  $190^{\circ}$ ) are described. *Nitro-iodisoquinoline* melts at  $140^{\circ}$ . On oxidation, iodoisoquinoline yields phthalic acid, showing that the iodine must be in the pyridine ring.

A. G. B.

**Pyridazine.** By ERNST TÄUBER (*Ber.*, 1895, **28**, 451—455).—

When phenazone,  $C_6H_4<\overline{N:N}>C_6H_4$  (*Abstr.*, 1892, 184), is suspended in water and oxidised with potassium permanganate on the water bath, it yields *pyridazinetetra-carboxylic acid*,



the *dipotassium salt* of which separates out when the filtered and concentrated solution is acidified with hydrochloric acid; it crystallises in white needles. If this salt is dissolved in cold, 15 per cent. hydrochloric acid, lustrous, rhombohedral crystals of a *monopotassium salt*, with  $1H_2O$ , soon separate. When heated for two hours with hydrochloric acid on the water bath, it loses carbonic anhydride, and, if the solution is concentrated and then diluted with water, *pyridazinedicarboxylic acid*, probably

$\begin{array}{c} \text{N}\cdot\text{CH}\cdot\text{C}\cdot\text{COOH} \\ \parallel \qquad \qquad \parallel \\ \text{N}\cdot\text{CH}\cdot\text{C}\cdot\text{COOH} \end{array}$ , separates; this crystallises in colourless prisms, darkens just above  $200^{\circ}$ , and melts and decomposes at  $205^{\circ}$ . When it is heated for 12 hours with 5 per cent.

hydrochloric acid at  $200^{\circ}$ , it yields *pyridazine*,  $\begin{array}{c} \text{N}\cdot\text{CH}\cdot\text{CH} \\ \parallel \qquad \parallel \\ \text{N}\cdot\text{CH}\cdot\text{CH} \end{array}$ ; this is a mobile, colourless oil which boils at  $208^{\circ}$  (corr.) and melts at  $-8^{\circ}$ ; it mixes with water in all proportions, and dissolves readily in alcohol, benzene, and ether, but not in light petroleum; it has a feeble odour suggestive of pyridine; it is neutral to litmus, and forms, for the most part, soluble salts; the *gold chloride compound*,  $C_4H_4N_2\cdot AuCl_3$  (the compound containing  $HCl$  in addition is unstable), however, separates even from dilute solutions in tiny, lemon-yellow needles which melt and decompose at about  $110^{\circ}$ ; mercuric chloride also forms an insoluble compound, but the platinochloride only separates from concentrated solutions of the base or its hydrochloride.

C. F. B.

**Pyrazole Series.** By R. VON ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 43—79).—A detailed account of researches of which notices have already been published (compare Abstr., 1893, i, 180, 367, 428, 611, 729; 1894, i, 145, 260, 349, 350, 385). A. H.

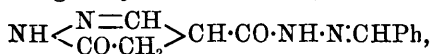
**Pyridazolones.** By R. v. ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 140—157; compare Abstr., 1893, i, 368, 732).—The preparation of pyridazolone\* has been already described (Abstr., 1893, i, 732). The compound boils at 169·5—171°, and is less prone to enter into reactions than is pyrazolone; with silver nitrate and ammonia in alcoholic solution, it gives a white, amorphous precipitate of the silver-derivative  $C_4H_5N_2OAg$ .

The derivatives of *pyridazolone-4-carboxylic acid*,



were previously mis-described as those of pyridazolone-3-carboxylic acid (*loc. cit.*). The acid itself is a crystalline mass which melts above 250°, and dissolves in the usual solvents; the *silver*, *calcium* (with  $1H_2O$ ), *barium* (with  $2\frac{1}{2}H_2O$ ), *lead*, *copper* (with  $1\frac{1}{2}H_2O$ ), *methylic* (m. p. 209—210°), and *ethylic* (m. p. 172°) salts are described.

*Pyridazolone-4-carbonylhydrazine*,  $NH < \begin{smallmatrix} N=CH \\ CO \cdot CH_2 \end{smallmatrix} > CH \cdot CO \cdot NH \cdot NH_2$ , and its corresponding *benzylidene* derivative,



have been described as 3-derivatives (*loc. cit.*). *Pyridazolone-4-carbonylisopropylenehydrazine*,  $NH < \begin{smallmatrix} N=CH \\ CO \cdot CH_2 \end{smallmatrix} > CH \cdot CO \cdot NH \cdot N : CMe_2$ , is obtained by dissolving the carbonylhydrazine in acetone; it crystallises from the solution in small needles and prisms which melt above 250°.

*3-Phenylpyridazolone*,  $NH < \begin{smallmatrix} N : CPh \\ CO \cdot CH_2 \end{smallmatrix} > CH_2$ , is prepared by heating ethylic  $\beta$ -benzoylpropionate with hydrazine hydrate in alcohol; it crystallises in large, flat needles, and melts at 145°; with benzaldehyde, it gives a red, easily soluble colouring matter; with nitrous acid, it yields a yellow, unstable *nitroso*-compound, which melts at 124°.

The author describes phthalazone (Abstr., 1893, i, 372) under the name *phenopyridazolone*. When heated with methylic iodide and methylic alcohol, it yields 1-*Methylphenopyridazolone*,  $C_6H_4 < \begin{smallmatrix} CH : N \\ CO \cdot NMe \end{smallmatrix}$ , which crystallises in laminæ or prisms, and melts at 114°; it has no acid properties. 1-*Ethylphenopyridazolone* crystallises in yellow laminæ and melts at 67—68°.

6-*Methoxyphenopyridazole*,  $C_6H_4 < \begin{smallmatrix} CH = N \\ C(OMe) : N \end{smallmatrix}$ , obtained from the interaction of 6-chlorophenopyridazole and sodium methoxide, crys-

\* Curtius has recently called derivatives of this class pyridazinones (this vol., 1, 247).

tallises in needles, and melts at 60—61°. The corresponding *ethoxy*-derivative melts at 29—31°.

1-Acetylphenopyridazolone, made by heating pyridazolone with acetic anhydride, crystallises in needles or prisms, and melts at 135°. *Pheno*-3-pyridazolonecarboxylic acid,  $C_6H_4 \cdot \begin{smallmatrix} C(COOH) : N \\ CO \text{ — } NH \end{smallmatrix}$  is obtained by

warming hydrazine hydrate with benzoylformic-orthocarboxylic acid in alcohol, melts above 250°; its *silver*, *copper* (with  $1H_2O$ ), and *methylic* salts are described.

3-Phenylphenopyridazolone (Abstr., 1893, i, 368) melts at 236°. 1-Methyl-3-phenylphenopyridazolone crystallises in laminæ, melts at 153°, and distils unchanged. 1-Ethyl-3-phenylphenopyridazolone melts at 109° and distils unchanged; 1-Acetyl-3-phenylphenopyridazolone melts at 178—179°.

3-Paratolylphenopyridazolone is prepared from paratoluoylbenzoic acid and hydrazine hydrate; it melts at 246°, and boils unchanged. 1-Methyl-3-paratolylphenopyridazolone crystallises in laminæ and melts at 170°. 3-Xylylphenopyridazolones are obtained when the three xyloylbenzoic acids are heated with hydrazine hydrate respectively; they melt above 250° and distil unchanged. 3-Naphthylphenopyridazolones have also been prepared.

The discovery of the isomeric alkyl derivatives of phenopyridazolone points to the existence of the tautomeric forms  $CO \cdot \begin{smallmatrix} NH \text{ — } N \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH$  and  $C(OH) \cdot \begin{smallmatrix} N \text{ — } N \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH$ . A distinction between pyrazolones and pyridazolones resides in their behaviour towards acids; the former are very stable, whilst the latter are easily split up into their parent substances. On the other hand, the pyridazolones can be distilled unchanged, whilst the pyrazolones, with the exception of pyrazolone itself and some of the simpler derivatives, are decomposed by distillation. The pyrazolones yield isonitroso-derivatives with nitrous acid, and azo-compounds with diazobenzene salts; the pyridazolones do not show either reaction.

A. G. B.

**Isomerism in the Pyrazole Series.** By R. v. ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 157—164).—The author agrees with Buchner (this vol., i, 192) that the phenylpyrazole which melts at 228° cannot be the 4-derivative, as Knorr and Sjollemma have stated it to be (Abstr., 1894, i, 546). Stolz (Abstr., 1894, i, 259) has expressed his opinion that the author's phenylpyrazolone (*Ber.*, 1893, 26, 2974), which melts at 155°, is not 1-phenyl-5-pyrazolone, but on grounds which are shown to be insufficient. If, as has been stated in certain German patent specifications, the so-called "pseudoanti-pyridines,"  $CO \cdot \begin{smallmatrix} NR_1 \cdot NPh \\ CH : CR_{11} \end{smallmatrix}$ , are poisonous, whilst the antipyridines,

$CO \cdot \begin{smallmatrix} NPh \cdot NR_1 \\ CH : CR_{11} \end{smallmatrix}$ , can be used as antipyretics, it becomes of great importance to be able to state the exact conditions under which compounds of the one and of the other class are produced.

C. Walker has prepared some pyrazolonesulphonic acids to which he ascribes the formula  $NPh < \begin{smallmatrix} N(SO_3H) \cdot CMe \\ CO \text{---} \text{---} \text{---} CR \end{smallmatrix}$  (Abstr., 1894, i, 475); this constitution is, however, exceedingly improbable, and the acids may be regarded as  $CO < \begin{smallmatrix} N(C_6H_4 \cdot SO_3H) \cdot N \\ CHR \text{---} \text{---} \text{---} CMe \end{smallmatrix}$  A. G. B.

**Aromatic Glyoxaline Compounds.** By RICHARD ANSCHÜTZ (*Annalen*, 1895, 284, 8).—Condensation of  $\alpha$ -hydroxyketones with thiocarbamide or ammonium thiocyanate, and with carbamide, has already been studied (Abstr., 1891, 725); the two following abstracts contain a further description of some of the products. M. O. F.

**Constitution of Products obtained from Benzoïn by the Action of Thiocarbamide or Ammonium Thiocyanate, and Carbamide.** By RICHARD ANSCHÜTZ and K. SCHWICKERATH (*Annalen*, 1895, 284, 9–25; compare Abstr., 1891, 725).—The orientation adopted by the authors for glyoxaline compounds is expressed by the

formula  $\begin{smallmatrix} \alpha R \cdot C \cdot \overset{\vee}{N} R \\ \beta R \cdot C \text{---} N \end{smallmatrix} > C \cdot R \mu$ .

$\alpha\beta$ -Diphenylglyoxaline  $\mu$ -hydrosulphide is obtained by condensing benzoïn with thiocarbamide or ammonium thiocyanate; the sodium salt forms lustrous, pale yellow leaflets. Solutions in acetic acid and alcohol exhibit a feeble, violet fluorescence. Treatment with concentrated sulphuric acid gives rise to evolution of sulphurous anhydride with development of a cherry-red coloration, a yellow, amorphous substance being formed on application of heat. This product again becomes red in a vacuum, but is decolorised on exposure to the air; it dissolves in alkali carbonates, and the solution becomes gelatinous.

$\alpha\beta$ -Diphenylglyoxaline  $\mu$ -methosulphide,  $\begin{smallmatrix} CPh \cdot NH \\ CPh \text{---} N \end{smallmatrix} > C \cdot SMe$ , is obtained from the hydriodide by treatment with boiling water. It crystallises from dilute alcohol in slender, white needles which melt at 233–234°; when it is fused with potash, the odour of mercaptan becomes perceptible. The hydriodide is formed when diphenylglyoxaline hydrosulphide is heated with methylic iodide and methylic alcohol on the water bath. It forms colourless crystals belonging to the rhombic system;  $a : b : c = 0.90199 : 1 : 0.72716$ . These crystals contain 1 mol.  $CH_3 \cdot OH$ , which is lost on exposure to the air. The hydriodide becomes reddish-brown at 180–190°, and melts at 201–202°.

$\alpha\beta$ -Diphenylglyoxaline  $\mu$ -ethosulphide, crystallises from alcohol in small, white needles, and melts at 181–182°.

$\alpha\beta$ -Diphenylglyoxaline  $\mu$ -disulphide,  $S_2(C_3N_2HPh_2)_2$ , is obtained from the sodium salt of  $\alpha\beta$ -diphenylglyoxaline  $\mu$ -hydrosulphide by the action of iodine, or by oxidation with potassium permanganate; it crystallises from alcohol in golden-yellow needles.

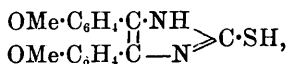
$\alpha\beta$ -Diphenylglyoxaline- $\mu$ -sulphonic acid is produced by further oxidation of the foregoing substance with potassium permanganate; it

melts at 271—273° with decomposition, and crystallises in white needles which contain 1H<sub>2</sub>O. The sulphonic acid resists the action of concentrated hydrochloric acid at 180—200°. The *potassium* salt forms small, white crystals.

When  $\alpha\beta$ -diphenylglyoxaline  $\mu$ -hydrosulphide is oxidised with nitric acid, the chief product is benzile; if, however, a mixture of sulphuric acid and potassium dichromate is used, dibenzoylcarbamide is formed. Dibenzoylcarbamide yields carbonic anhydride, benzonitrile, and benzamide when heated at 205—210°.

*Diphenylacetyleneurein*, or *tolaneurein*,  $\begin{matrix} \text{CPh}\cdot\text{NH} \\ \parallel \\ \text{CPh}\cdot\text{NH} \end{matrix} > \text{CO}$ , is soluble in warm aqueous soda, and also resembles  $\alpha\beta$ -diphenylglyoxaline  $\mu$ -hydrosulphide in its behaviour towards concentrated sulphuric acid; it resists, however, the action of acetic chloride, and does not form additive products with methylic and ethylic iodides. Potassium permanganate oxidises it to a mixture of benzoic and benzilic acids, whilst chromic acid gives rise to dibenzoylcarbamide.

$\alpha\beta$ -Diparamethoxyphenylglyoxaline  $\mu$ -hydrosulphide,



is produced by condensation of anisoïn with thiocarbamide; it melts at 280°, and becomes yellowish-green on treatment with concentrated sulphuric acid.

*Diparamethoxytolaneurein*,  $\begin{matrix} \text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{NH} \\ \parallel \\ \text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{NH} \end{matrix} > \text{CO}$ , is obtained by condensing anisoïn with carbamide; it crystallises from alcohol in small, white needles, and remains unchanged at 280°. M. O. F.

**Action of Monosubstituted Derivatives of Carbamide and Thiocarbamide on Benzoin.** By RICHARD ANSCHÜTZ and HERMANN MÜLLER (*Annalen*, 1895, **284**, 25—35).— $\alpha\beta$ -Diphenyl-*v*-ethylglyoxaline

$\mu$ -hydrosulphide,  $\begin{matrix} \text{CPh}\cdot\text{NEt} \\ \parallel \\ \text{CPh}-\text{N} \end{matrix} > \text{C}\cdot\text{SH}$ , is prepared by heating a mixture

of ethylthiocarbamide, benzoin, and alcohol for four hours at 180—190°; it crystallises in yellowish needles, and undergoes no change at 240°.  $\alpha\beta$ -Diphenyl-*v*-ethylglyoxaline  $\mu$ -methosulphide melts at 106°.

$\alpha\beta$ -Diphenyl-*v*-allylglyoxaline  $\mu$ -hydrosulphide crystallises in needles, and remains unchanged at 240°; the *potassium* salt forms lustrous leaflets.

$\alpha\beta$ -Triphenylglyoxaline  $\mu$ -hydrosulphide is obtained by condensing benzoin with phenylthiocarbamide. It crystallises from alcohol or glacial acetic acid in white leaflets, and does not melt below 290°; the solutions in these two solvents exhibit a violet fluorescence. The *potassium* salt forms stellate groups of colourless needles.

$\alpha\beta$ -Triphenylglyoxaline  $\mu$ -methosulphide crystallises from alcohol in colourless needles and melts at 177°; on fusing it with potash, the odour of mercaptan becomes perceptible.  $\alpha\beta$ -Triphenylglyoxaline  $\mu$ -ethosulphide forms yellow crystals.  $\alpha\beta$ -Diphenyl-*v*- $\beta$ -naphthylglyoxaline  $\mu$ -hydrosulphide is prepared by heating a mixture of  $\beta$ -naphthyl-

thiocarbamide, benzoïn, and alcohol for five hours at 200—210°; it crystallises from alcohol in small, colourless needles.

*Diphenylacetylenemethylurein*,  $\begin{array}{c} \text{CPh} \cdot \text{NMe} \\ || \\ \text{CPh} - \text{N} \end{array} > \text{CO}$ , is produced when benzoïn is heated with methylcarbamide and alcohol for several hours at 270—280°. It forms white needles, and remains unchanged at 290°. *Diphenylacetylenephnylurein* also undergoes no change at 290°, and *diphenylacetylene-β-naphthylurein*, which crystallises in grey needles, becomes brown at 280°. M. O. F.

**Phenometadiazine Derivatives.** By STEFAN NIEMENTOWSKI (*Ber.*, 1895, 28, 443).—The author points out that between the melting point of β-ethyl-α-hydroxyphenometadiazine and of pheno-β-isopropyl-α-hydroxymetadiazine as determined by him, and the observations recorded in the recent paper of Bischler and Lang (this vol., i, 250), a wide discrepancy exists; the compounds in question may occur in two isomeric forms. M. O. F.

**Orthamidobenzylamine.** By MAX BUSCH (*J. pr. Chem.*, 1895, [2], 51, 113—139).—The majority of the reactions and compounds described in this paper has already received notice (*Abstr.*, 1894, i, 146, 625; this vol., 31).

Oxidation of ketotetrahydroquinazoline and of thiotetrahydroquinazoline with potassium permanganate, produces benzoylenecarbamide. When reduced by sodium in alcohol, thiotetrahydroquinazoline yields tetrahydroquinazoline, the *hydrochloride*,  $\text{C}_8\text{H}_{10}\text{N}_2 \cdot \text{HCl}$ , of which is not dissociated by water, as are those of its substituted derivatives, and melts at 192°; the *platinochloride* is described.

Orthamidobenzylmethylamine *hydrochloride*,  $\text{C}_8\text{H}_{12}\text{N}_2 \cdot 2\text{HCl}$ , crystallises in lustrous laminae, and melts at 217°.

3-Methylthiotetrahydroquinazoline,  $\text{C}_8\text{H}_9 < \begin{array}{c} \text{NH} \cdot \text{CS} \\ | \\ \text{CH}_2 \cdot \text{NMe} \end{array}$ , prepared by heating orthamidobenzylmethylamine with carbon bisulphide, crystallises in white needles, melts at 181°, and dissolves easily in benzene and chloroform, but only sparingly in ether and water.

*Methylidihydro-β-phenotriazinehydrochloride* crystallises in large, pale, yellow prisms, and melts at 146—147°, evolving gas; the *platinochloride* and *picrate* are described.

Orthamidobenzylethylamine *hydrochloride*,  $\text{C}_9\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ , melts at 210°; the *oxalate* at 184°. When the base is treated in ethereal solution with a 20 per cent. solution of phosgene in toluene, 3-ethylketotetrahydroquinazoline is obtained; this crystallises in white needles, and melts at 142°.

Ethyl diketotetrahydroquinazoline,  $\text{C}_8\text{H}_7 < \begin{array}{c} \text{NH} \cdot \text{CO} \\ | \\ \text{CO} \cdot \text{NEt} \end{array}$ , is the product of the oxidation of ethylthiotetrahydroquinazoline by potassium permanganate; it crystallises in lustrous, white needles, melts at 188°, and dissolves in hot absolute alcohol and in aqueous alkalis, to which it imparts a blue fluorescence. It is, perhaps, identical with Söderbaum's phenoethyl diketometadiazine (*Abstr.*, 1890, 1254).



1 : 3-Methylethylthiotetrahydroquinazoline,  $C_6H_4 \begin{smallmatrix} \text{NMe} \cdot \text{CS} \\ \text{CH}_2 \cdot \text{NEt} \end{smallmatrix}$ , is prepared by heating ethylthiotetrahydroquinazoline with methylic alcohol and methylic iodide. It forms a yellow oil which gradually crystallises from alcohol in square tablets, melting at  $65^\circ$ .

The *hydrochloride*,  $C_9H_{11}N_3 \cdot HCl$  (m. p.  $141^\circ$ ), *platinochloride*, *hydrobromide* (m. p.  $151^\circ$ ), *sulphate*,  $C_9H_{11}N_3 \cdot H_2SO_4$  (m. p.  $150^\circ$ ), and *picrate* (m. p.  $150^\circ$ ) of  $\beta$ -phenomethylidihydrotriazine are described.

A. G. B.

**Orthamidobenzylamine.** By MAX BUSCH (*J. pr. Chem.*, 1895, [2], 51, 257—284; compare Abstr., 1894, i, 146).—*Orthonitrotribenzylamine* is formed when benzylic chloride is heated with ortho-nitrobenzylamine (2 mols.); it crystallises in large, sulphur-yellow prisms, and melts at  $56^\circ$ . The *hydrochloride* melts at  $190^\circ$ , and the *platinochloride* at  $200^\circ$ . *Orthonitrodibenzylamine* is obtained by heating benzylic chloride with nitrobenzylamine in alcoholic solution. It is a yellowish oil, and its *hydrochloride* melts at  $225^\circ$ .

*Orthonitrobenzylanilidophenylsulphone*,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot SO_2Ph$ , is obtained by heating nitrobenzylamine with benzenesulphonic chloride, and crystallises in needles melting at  $143^\circ$ .

*Orthamidobenzylanilidophenylsulphone* crystallises in matted needles, and melts at  $139$ — $140^\circ$ . It does not yield an anhydro-compound when heated alone or with dehydrating agents. Hydrochloric acid decomposes it with formation of phenylsulphanilide.

Phenylketotetrahydroquinazoline (Abstr., 1892, 1495) and phenylthiotetrahydroquinazoline are converted by oxidation with potassium permanganate into *phenyldiketotetrahydroquinazoline*,  $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NPh} \end{smallmatrix}$ , which crystallises in arborescent needles, and melts at  $272^\circ$ . Phenylthiotetrahydroquinazoline is converted by methylic iodide into the *hydriodide of methylphenylthiotetrahydroquinazoline*, which melts and decomposes at  $225^\circ$ . The free base forms compact crystals melting at  $92^\circ$ , and is strongly basic, whereas the unmethylated quinazoline is indifferent towards acids.

*Orthonitrobenzylparatoluidophenylsulphone* forms compact yellow crystals which melt at  $124^\circ$ . The corresponding *amido-compound* crystallises in lustrous, white needles, and melts at  $132^\circ$ .

*Orthamidobenzylorthotoluidine*,  $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Me$ , crystallises in flat, lustrous needles melting at  $94^\circ$ . The *hydrochloride* melts at  $180$ — $181^\circ$ . During the reduction of orthonitrobenzylorthotoluidine, *orthotolylindazole*,  $C_6H_4 \begin{smallmatrix} \text{N} - \\ \text{CH} \end{smallmatrix} > N \cdot C_6H_4Me$ , which crystallises

in slender needles, melting at  $80$ — $81^\circ$ , is obtained accompanied by *orthazobenzylorthotoluidine*,  $N_2(C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4)_2$ , which forms red crystals melting at  $160^\circ$ . *Orthamidobenzylorthotoluidine* does not appear to react with nitrous acid to form a phenotriazine. *Orthotolylketotetrahydroquinazoline* crystallises in lustrous, white plates, and melts at  $189$ — $190^\circ$ . *Orthotolylthiotetrahydroquinazoline* forms flat, white needles, and melts at  $202^\circ$ . *Orthotolyl diketotetrahydroquinazoline*, obtained by oxidation from the foregoing compounds, forms

white crystals melting at 241—242°. *Orthonitrobenzylorthotolylnitrosamine* crystallises in yellowish, vitreous needles, and melts at 64—65°. The *amido-compound* melts at 86—87°. Acetyldihydro- $\beta$ -phenotriazine is decomposed by hydrochloric acid with formation of *orthochlorobenzylacetamide*, which crystallises in white, lustrous needles melting at 79—80°. The *hydrochloride* also forms white needles. Both acetyldihydrophenotriazine and its salts form azo-compounds by condensation with amido-compounds and phenols. With  $\beta$ -naphthol, a compound which crystallises in slender, orange-red needles is formed, whilst the product obtained from dimethylaniline is dark yellow, and that from metaphenylenediamine, golden-yellow.

Benzoyldihydro- $\beta$ -phenotriazine is decomposed by the halogen hydr-acids with formation of the corresponding substituted benzylbenzamides. *Orthochlorobenzylbenzamide* forms colourless, lustrous needles melting at 116—117°. *Orthobromobenzylbenzamide* crystallises in plates melting at 134°, whilst *orthiodobenzylbenzamide* also forms plates which melt at 154°. *Orthohydroxybenzylbenzamide* may be obtained by boiling the benzoyldihydrophenotriazine hydrochloride with water, and forms white needles melting at 139—140°. The benzoyltriazine condenses with  $\beta$ -naphthol to form the compound  $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , which crystallises in silky, purple-red needles melting at 215°. On reduction, it is converted into *ortbamidobenzylbenzamide* and *amidonaphthol*. The *compound* with dimethylaniline is orange-yellow, and melts at 140°; whilst that with metaphenylenediamine is also orange-yellow, and decomposes and melts at 160°. A. H.

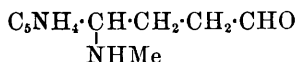
**New Synthesis of Triazole and its Derivatives.** By GUIDO PELLIZZARI (*Gazzetta*, 24, ii, 222—229).—The alkylic derivatives of formylhydrazide react readily with formamide yielding mono-substituted triazoles and water. In the preparation of triazole or of 1-phenyltriazole, formamide is slowly distilled with formylhydrazine or formylphenylhydrazine respectively; the triazole distills, and a good yield is obtained on purification. In the preparation of triazole, a poorer yield is obtained by distilling hydrazine hydrate or hydrochloride with formamide or ammonium formate, or by heating hydrazine hydrochloride with ammonium chloride or sodium formate, inasmuch as secondary reactions occur to a greater extent than in the first method described above. W. J. P.

**Nicotine.** By ADOLF PINNER (*Ber.*, 1895, 28, 456—465; compare Abstr., 1891, 473, and 1892, 1010).—It is shown that oxynicotine,  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}$  (not  $\text{H}_{12}$ ), is not the primary product of the oxidation of nicotine with hydrogen peroxide, but is formed by condensation from an aldehyde first formed. When oxynicotine is heated for 8—10 hours at 140° with saturated baryta water, and the product distilled with steam, the distillate contains nicotine and pseudo-nicotine oxide, better named *nicotol*. From the residue, an oil can be isolated, which decomposes when heated at about 165° under 50 mm. pressure; by fractional crystallisation of the mixed picrates

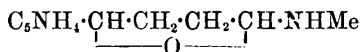
obtained from the oily distillate, nicotine and *nicotone*, an isomeride of oxynicotine and nicotol, were isolated. Nicotone is a colourless, strongly basic oil, which boils at  $253^{\circ}$ ; it has no reducing action. The picrate,  $C_{10}H_{14}N_2O_2 \cdot 2C_6H_3N_3O_7$ , melts at  $184^{\circ}$ , and is readily soluble in hot, but only sparingly in cold, water.

When metanicotine is treated with methylic iodide (3 mols.) in methyl alcoholic solution at the ordinary temperature, a *methiodide* of *methylnicotine*,  $C_{10}H_{13}MeN_2 \cdot 2MeI$ , is obtained; this crystallises in colourless needles, and melts at  $189^{\circ}$ .

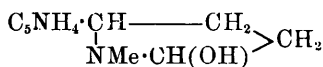
The following formulæ are assigned to the substances described in this and the previous papers. Brühl finds that those given for nicotine and metanicotine are in harmony with the optical constants of these substances as determined by him.



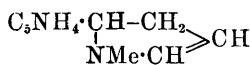
Aldehyde (Oxynicotine).



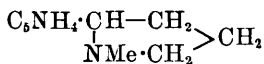
Nicotone.



Nicotol (pseudonicotine oxide).



Dehydronicotine.



Nicotine.



Metanicotine.

C. F. B.

**Nicotine Oxalate and other Salts.** By H. PARENTY and E. GRASSET (*Compt. rend.*, 1894, 119, 1273—1276).—Nicotine quadroxalate,  $C_{10}H_{14}N_2 \cdot 2H_2C_2O_4$ , is readily obtained in nacreous lamellæ by adding excess of oxalic acid to the normal oxalate,  $2C_{10}H_{14}N_2 \cdot H_2C_2O_4$ . In order to prepare it on a large scale, the aqueous extract from tobacco residues is made alkaline, and allowed to fall in the form of fine rain through light petroleum, contained in a series of six vertical tubes in a special apparatus, the liquid passing through the six tubes in succession. The light petroleum is then vigorously agitated with the proper proportion of finely-powdered oxalic acid, and the quadroxalate is dried.

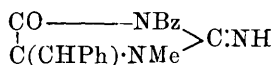
Nicotine quadroxalate is very soluble in water and in alcohol. When the anhydrous salt is heated, it melts at  $110^{\circ}$ , and begins to decompose with violent evolution of gas at  $113.5^{\circ}$ . At  $160^{\circ}$ , it yields the normal oxalate, and at  $250^{\circ}$  pure nicotine. In order to obtain the base, it is best, after the initial evolution of gas has moderated, to collect the distillate, and rectify it after adding calcium or lead oxide. The quadroxalate can be employed for the same purposes as nicotine. The fatal dose of free nicotine, when injected hypodermically, is 20 to 21 milligrams per kilo. of body weight, but this rises to 70 milligrams (or 150 milligrams of the quadroxalate) when the nicotine is in combination. It follows that the quadroxalate has only one-eighth of the poisonous effect of an equal weight of free nicotine. The physiological effects, though less intense, are identical.

C. H. B.

**Diacetylcreatine and Benzylideneacetylcreatinine.** By EMIL ERLÉNMEYER, jun. (*Annalen*, 1895, **284**, 49—52).—*Diacetylcreatine*,  $C_4H_7O_2N_3Ac_2$ , is obtained by dissolving creatine in excess of warm acetic anhydride and evaporating the liquid after addition of water; it crystallises from alcohol in slender needles, which melt at  $165^\circ$ .

*Benzylideneacetylcreatinine*,  $C_{13}H_{13}O_2N_3$ , is formed when creatine is heated on the water bath with benzaldehyde (1 mol.) and acetic anhydride (3 mols.); it crystallises from glacial acetic acid in small, golden-yellow needles, and melts at  $213^\circ$ .

The structure of the two foregoing compounds is probably represented by the expressions

$$\begin{array}{c} NMe \cdot C(NHAc) \cdot NH \\ | \\ CH_2 \cdot COOAc \end{array} \quad \text{and}$$


respectively.

M. O. F.

**$\beta$ -Hydroxycinchonine.** By EMILIE JUNGFEISCH and E. LÉGER (*Compt. rend.*, 1894, **119**, 1268—1270).— $\beta$ -Hydroxycinchonine (see Abstr., 1889, 906) is formed, together with  $\alpha$ -hydroxycinchonine, by the prolonged action of sulphuric acid diluted with an equal weight of water on cinchonine, at  $120^\circ$ . The  $\alpha$ -compound is separated in the form of basic hydrochloride, which is only slightly soluble, and the  $\beta$ -derivative in the form of basic succinate. Final purification is effected by conversion into diacetyl derivatives, that derived from  $\beta$ -hydroxycinchonine being only very slightly soluble in ether.

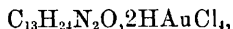
$\beta$ -Hydroxycinchonine crystallises from strong alcohol in small, colourless, anhydrous, acicular prisms which begin to decompose at  $250^\circ$  and melt at  $273^\circ$  (corr.). It is somewhat more dextrogyrate than the  $\alpha$ -compound; in absolute alcohol at  $17^\circ$ ,  $[\alpha]_D = +188.8^\circ$ ; in water containing 2 mols. HCl at  $15^\circ$ ,  $[\alpha]_D = +228^\circ$ ; and with 4 mols. HCl,  $[\alpha]_D = +228.33^\circ$ .

$\beta$ -Hydroxycinchonine is almost insoluble in water, but in dilute solutions precipitation by an alkali takes place very slowly; it is soluble in alcohol, especially on heating, but is less soluble in acetone than its isomeride; it dissolves in chloroform, especially at the moment of its liberation from one of its salts, although the excess of base thus dissolved gradually separates in a crystalline form. The base is alkaline to litmus and phenolphthalein, and forms two series of salts, normal  $C_{38}H_{22}N_2O_4 \cdot 2HR'$  and  $C_{38}H_{22}N_2O_4 \cdot HR'$ . They crystallise well in prisms or needles, and with the exception of the basic iodide, platinochloride, cadmiochloride and basic oxalate, basic succinate and basic tartrate, are soluble in water, especially on heating. The *platinochloride* forms orange-yellow needles; the other salts are white.

C. H. B.

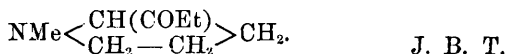
**Hygrine and Hygric acid.** By CARL T. LIEBERMANN and GUSTAV CYBULSKI (*Ber.*, 1895, **28**, 578—585).—In addition to the “low-boiling hygrine” and “high-boiling hygrine,” a third alkaloid has been isolated from Bolivian cusco leaves, and the name *cusckhygrine* suggested for it. It is a colourless oily liquid, boils at  $185^\circ$  (32 mm.), has a sp. gr. of 0.9767 at  $17^\circ/17^\circ$ , and is optically inactive. The

base,  $C_{13}H_{24}N_2O$ , is isolated by means of the crystalline *nitrate*. The *hydrochloride*,  $C_{13}H_{24}N_2O \cdot 2HCl$ , and the *aurochloride*,

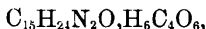


are crystalline, the former is hygroscopic. The *platinochloride* has also been obtained. "Low-boiling hygrine" boils at  $92-94^\circ$  (20 mm.) and  $111-113^\circ$  (50 mm.); sp. gr. = 0.935 at  $17^\circ/4^\circ$ ;  $\alpha_D = -1.3^\circ$ .

Hygric acid melts at  $164^\circ$ , but retains water of crystallisation even when deposited from alcohol, hence the lower melting points previously observed (Abstr., 1891, 586). When the anhydrous acid is heated slightly above its melting point, carbonic anhydride is copiously evolved, and a mixture of bases is obtained equal to 46 per cent. of the original acid. The constituent of lowest boiling point is *n*-methylpyrrolidine, which is a strong base and absorbs water and carbonic anhydride from the atmosphere; its vapour, when inhaled, produces violent headache. The *platinochloride*,  $(C_5H_{11}N)_2H_2PtCl_6$ , melts at  $233^\circ$ . The *picrate*, *potassiomeric iodide*, and *mercurochloride* crystallise in needles; the first two are yellow. The above base differs from piperidine in giving no nitroso-derivative, no compound with carbon bisulphide, and no compound corresponding with benzoyl-piperidine; it is a tertiary base, and readily combines with methylic iodide. Determinations by Herzig and H. Meyer's method show that *n*-methylpyrrolidine, "low-boiling hygrine," and hygric acid all contain one NMe group, cuskhygrine contains two. The readiness with which carbonic anhydride is eliminated from hygric acid suggests that the carboxyl group is in the  $\alpha$ -position, "low-boiling hygrine," therefore, probably has the formula



**Alkaloids of *Lupinus Albus*.** By ARTURO SOLDAINI (*L'Orosi*, 17, 253-262; compare Abstr., 1893, i, 379, 739).—The deliquescent dextrorotatory alkaloid extracted from the seeds of *Lupinus albus* yields a deliquescent *hydrogen sulphate*,  $C_{15}H_{24}N_2O \cdot H_2SO_4 \cdot H_2O$ , melting at  $178-179^\circ$ ; the *normal sulphate*,  $(C_{15}H_{24}N_2O)_2 \cdot H_2SO_4$  (?), crystallises in micaceous scales melting at  $82-83^\circ$ . The *hydrogen tartrate*,



crystallises in hemihedral, anorthic crystals melting at  $192-193^\circ$ ;  $a : b : c = 1.0257 : 1 : 0.8160$ .  $\alpha = 89^\circ 0'$ ,  $\beta = 95^\circ 13'$ ,  $\gamma = 90^\circ 39'$ . An *iodine* additive compound,  $C_{15}H_{24}N_2OI_3$ , was also obtained in brown scales melting at  $196-197^\circ$ .

The isomeric inactive alkaloid also yields a *hydrogen sulphate* melting at about  $186^\circ$ , but the normal sulphate is a syrup. The *hydrogen tartrate*,  $C_{15}H_{24}N_2O \cdot H_6C_4O_6 \cdot 2\frac{1}{2}H_2O$ , is obtained in hemimorphic monosymmetric crystals melting and decomposing at  $184-185^\circ$ ;  $a : b : c = 0.9157 : 1 : 1.0432$ .  $\beta = 82^\circ 52'$ .

Lupinidine does not seem to occur in the seeds of *Lupinus albus*.

W. J. P.

**Pereiro Bark.** By OSWALD HESSE (*Annalen*, 1895, **284**, 195—196; compare Abstr., 1894, i, 155, also Freund and Fauvet, this vol., i, 194).—The author has not met with a second variety of pereiro bark, and is of opinion that the source of vellosine cannot strictly be regarded as such. M. O. F.

**Pectase and the Pectic Fermentation.** By GABRIEL BERTRAND and ALFRED MALLÈVRE (*Compt. rend.*, 1894, **119**, 1012—1014, and 1895, **120**, 110—112).—According to Fremy, pectase is an unorganised ferment which causes the coagulation of vegetable juices rich in pectin, and which exists in a soluble form in the roots of the carrot and the beet, and in an insoluble form in apples and other acid fruits. The authors find that the coagulum produced by the action of the juice of carrots on a solution of pectin consists of calcium pectate and is not pectic acid as has been generally supposed; it is insoluble in dilute solutions of alkalis, but dissolves very readily in dilute hydrochloric acid, and the solution contains calcium which is not precipitated on adding excess of ammonia.

If the whole of the calcium is precipitated from the juice of carrots by adding exactly the required amount of potassium oxalate, and if pectin is entirely freed from calcium by treatment with dilute alcohol acidified with hydrochloric acid, no coagulation takes place on mixing the two solutions. The addition of a small quantity of a calcium salt causes almost immediate gelatinisation. Neither pectase nor calcium salts alone are able to coagulate pectin; the simultaneous presence of the two is essential. Barium and strontium salts have the same effect as calcium salts.

The action of the juice of carrots on a solution of pectin is greatly retarded by the presence of inorganic acids, and by malic, citric, or oxalic acid. With 0.088 gram of hydrochloric acid in 100 c.c., gelatinisation does not take place until after 40 hours; and with 0.1 gram of acid, the liquid does not gelatinise at all. It is noteworthy that many fruits at certain stages of their development contain proportions of acid considerably greater than those employed in these experiments.

The effect of acids is reduced by the presence of an increased proportion of pectase or of calcium salts. Pectic fermentation, in fact, depends on the relative proportions of pectase, calcium salts, and free acid. There is little doubt that this retarding influence of acids led Fremy to conclude that pectase is not present in the juice of apples and other acid fruits, and to suppose that it was present in an insoluble form in the solid part of the pulp. As a matter of fact, if the juice from apples, pears, &c., at various stages of development, is carefully neutralised, it readily coagulates the juice of carrots. The readier action of the pectase left in the pulp is due to the fact that the greater part of the acid has been removed. The authors find that the pectase precipitated by alcohol will redissolve in water if sufficient time is allowed and has not really become insoluble as Fremy supposed. The apparent inactivity of the precipitated pectase is due to the fact that the calcium salts which originally accompanied it are, to a large extent, left in the alcoholic liquid. C. H. B.

**The Blue Iodide of Cholic acid.** By FRITZ W. KÜSTER (*Zeit. physikal. Chem.*, 1895, **16**, 156—163).—In order to determine whether the blue compound of iodine and cholic acid is a true compound or a solid solution, a solution of the acid in alcohol was prepared, iodine added, and the cholic acid precipitated by water. The partition ratio of the iodine in the cholic acid and aqueous alcohol was then determined. The ratio for different amounts of iodine was not constant. When the quantity of iodine in the acid reached 28 per cent. it remained approximately constant. The blue substance appears to be therefore a compound which is easily and completely dissociated by water, and the solution tension of the iodine against water is equal to that of the iodine in a solution containing 0.020 gram per 100 c.c. The partition ratios of iodine in alcohol and carbon bisulphide were also determined, the presence of the acid being shown to have little effect on these numbers. The compound is, therefore, neither a solid solution nor a true chemical compound but a crystal structure analogous to that which the acid forms with water, alcohol, &c. L. M. J.

**Iodine Compounds of Starch and of Cholic acid.** By FRANZ MYLIUS (*Ber.*, 1895, **28**, 385—390; compare *Abstr.*, 1887, 568, and Küster, this vol., i, 199).—Cholic acid has already been shown to yield blue compounds of the type  $(C_{24}H_{40}O_5)_x \cdot I_2 + nH_2O$  when it is treated with solutions of iodine in aqueous hydriodic acid or metallic iodides. It is now shown that if these solutions are concentrated as regards the iodide, a brown crystallised compound,  $C_{24}H_{40}O_5 \cdot I_2$ , is formed, into the composition of which neither hydriodic acid nor metallic iodides enter. This compound is regarded as a true iodine additive compound of cholic acid, the others are compounds of iodine with the hydriodide, &c., of the acid. The brown compound is best made by dissolving cholic acid and iodine (1 mol. of each) in alcohol, and diluting the solution with water. It is converted into the blue compound by the action of reducing agents or of hydriodic acid or metallic iodides in the presence of water, and it is formed from the blue compound when the latter is treated with concentrated iodine solutions.

Starch, under similar circumstances, also yields a brown compound, ( $? C_{24}H_{40}O_{20} + I_2$ ), in addition to the blue compound already known, and so do the amyloids obtained from cellulose. C. F. B.

**Phosphorcarnic acid.** By MAX A. SIEGFRIED (*Ber.*, 1895, **28**, 515—519).—The author has previously shown (this vol., i, 76) that the muscles contain a compound termed phosphorcarnic acid which is easily separated by means of its iron compound, “carniferrin.” By the action of baryta water, the acid is resolved into phosphoric acid and carnic acid,  $C_{10}H_{15}N_3O_6$ , which is identical with anti-peptone. The alcoholic mother liquor obtained after the deposition of the carnic acid contains succinic acid and sarcolactic acid; the former gave a soluble barium salt probably derived from the labile modification of the acid. By the action of sodium carbonate on carniferrin, and treatment of the filtrate with baryta water, phosphoric acid, carnic acid, and a sugar are formed; the latter readily reduces Fehling's

solution, and yields an osazone, but has not yet been identified. It is very probable that sarcolactic acid is formed by the hydrolysis of phosphorcarnic acid, and attempts will be made to prove this. The term *nucleon* is suggested for compounds, such as phosphorcarnic acid, which are allied to the nucleins but contain peptone instead of albumin. Following Kossel, it is necessary to distinguish between *true nucleons* and *paramucleons*; phosphorcarnic acid belongs to the latter class and may be termed *muscle nucleone*.

Experiments on dogs have shown that phosphorcarnic acid is absorbed during muscular activity; in one instance three times as much was present in inactive muscles as in fatigued ones. This explains the appearance of phosphoric acid in the muscles as the result of their activity. As carnic acid has not hitherto been detected in the muscles, it is either absorbed during muscular growth or it contributes by its oxidation to muscular energy.

The formation of ammonium thiosulphate from ammonium sulphide and carnic acid which has been previously suggested as a test for the latter, only applies when colourless, recently prepared, ammonium sulphide is employed, as the yellow compound when evaporated alone yields ammonium thiosulphate. J. B. T.

**Coagulation of Colloïds.** By JOHN W. PICKERING (*Proc. Physiol. Soc.*, 1895, 5—6).—Colloïd substances prepared by Grimaux were examined, the three principal being those formed by the action of phosphorus pentachloride on metamidobenzoic acid, and that formed by the action of phosphorus oxychloride on aspartic acid.

In each case, the substance is a white amorphous powder readily soluble in ammonia; on evaporating the ammonia, brownish plates remain not unlike dried serum albumin. They are slightly soluble in distilled water in the cold, readily on heating. The solution is opalescent, and does not coagulate on heating; but if one or two drops of a 1 per cent. solution of a soluble salt of either barium, strontium, or calcium, is added, pronounced coagulation begins on heating to 70°. A few drops of a saturated solution of sodium chloride will also induce coagulation at 70°. If a more dilute solution of these salts be added, the passage of a current of carbonic or sulphurous anhydride through the solutions will determine their coagulability.

Sodium sulphate, and potassium acetate retard the coagulation. Glycerol prevents heat coagulation, but the passage of a current of carbonic anhydride through the solution will restore coagulability. The "colloïde aspartique" gives a violet reaction with copper sulphate and potash, a yellow with nickel sulphate and potash, and a red-brown with cobalt sulphate and potash. Each colloïd gives a well marked xanthoproteic reaction, and each is precipitated by trichloroacetic acid and by salicylsulphonic acid, the latter precipitate being coagulated on heating. This remarkable resemblance to proteid is accentuated by the fact that intravascular injection into a rabbit of a few c.c. of a 1 per cent. solution causes complete intravascular coagulation. W. D. H.



**Uroerythrin.** By ARCHIBALD E. GARROD (*J. Physiol.*, 1895, **17**, 439—450).—The colouring matter of pink urate sediments has been termed uroerythrin, but its nature has never been satisfactorily determined. B. Mester's opinion that it is a scatole derivative is considered to be untenable. Reale's view (*Rivista Clin. e Terapeut.*, 1891) that it is urobilin has also been shown to be incorrect by Riva (*Gaz. med. di Torino*, 1892, **43**, 1 and 923) and Zoja (*Archiv. Ital. di Clin. Med.*, 1893, **32**, 63). The principal results of Riva and Zoja's work is as follows:—The sediment is washed upon the filter-paper with ice cold water, dried, and soaked in absolute alcohol; it is next dissolved in warm water, and extracted with amylic alcohol, which takes up all the uroerythrin, and after filtration is clear. Cold absolute alcohol dissolves isolated uroerythrin readily, but does not extract the pigment from urate sediments. The solutions have a ruddy orange tint; they absorb the blue end of the spectrum, but dilute solutions show two absorption bands united by shading between E and F. Strong sulphuric and hydrochloric acid impart a pink colour to the solutions, but acetic acid produces no immediate change. Caustic alkalis destroy the pigment and change its colour to green. Not unfrequently a play of colours is observed when an alkali is added; the green solution shows no absorption bands. Solutions of uroerythrin are rapidly decolorised by actinic light, which, however, has little effect on the solid pigment and none at all on pink urate sediments. The pigment is precipitated by salts of lead, barium, calcium, and tin, and the precipitate is pink. Solid uroerythrin leaves no ash on combustion, and gives off only a small quantity of ammonia when heated with caustic potash.

The present research shows that the colour of urate sediments varies, owing to the fact that other pigments take part in the coloration. These other pigments are urochrome, hæmatoporphyrin, bile pigments and chrysophanic acid (found in the urine of patients taking rhubarb, or senna).

In support of the hypothesis that the uroerythrin in urate sediments is in combination, it is found that the sediment constantly shows a definite absorption band on the blue side of the D line; the deposit is examined on filter-paper by reflected light, or the paper may be dried, oiled, and then examined by transmitted light. Uroerythrin itself in solid form or solution does not show this band.

The following new process for the extraction of uroerythrin from the sediment is described. The sediment is washed off a filter-paper by a stream of cold water, and gentle warmth applied until it dissolves. This solution is saturated with ammonium chloride, and the ammonium urate thus precipitated carries all the uroerythrin down with it; the filtrate generally shows a urobilin band. The precipitate is washed with a saturated solution of ammonium chloride until the washings have no longer a yellow tint; the filter-paper, with its deposit, is then soaked in warm alcohol for several hours in the dark, and on filtering, a more or less concentrated solution of uroerythrin is obtained. To this, twice its bulk of water is added, and the mixture is shaken with chloroform, which becomes yellow by removing impurities; this operation is repeated several times. Chloro-

form is then added together with a drop of acetic acid, when a chloroformic solution of uroerythrin is obtained. The chloroform is evaporated at a low temperature, and the solid residue dissolves readily in absolute alcohol. The quantity of pigment obtained even from deeply coloured solutions is very small. It leaves no ash, and contains no iron. The spectrum of the solution is that already given, and first accurately described by MacMunn. Its reactions are uncertain, as it is so rapidly bleached by light; strong sulphuric acid causes a brilliant carmine colour with a dark absorption band on the blue side of D; on exposure to light, it becomes greenish-yellow. If hydrochloric acid is used instead, a pink is obtained giving an ill-defined shading from  $\lambda 608$ — $517$ ; it also becomes greenish on exposure to light. Phosphoric acid gives a salmon pink with two bands very like those of uroerythrin, but nearer the red; it is less rapidly decolorised by light than the original uroerythrin. In the case of all these acid products, the original colour and spectrum are restored by dilution with alcohol, and all are soluble in chloroform. Alkalis cause a play of colours, the final product being green. Acidification with acetic acid restores the uroerythrin, except after the green stage has been reached. The precipitation produced by metallic salts is considered to be due to precipitation of urates which carry down the pigment with them.

Clinical evidence points strongly to the liver as the probable seat of formation of uroerythrin, but no clue has as yet been obtained indicating a relation to, or derivation from the pigments of blood or bile.

W. D. H.

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## Organic Chemistry.

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**Carbonyl Bromide and Chlorobromide.** By J. ADOLPHE BESSON (*Compt. rend.*, 1895, **120**, 190—192).—When a solution of aluminium bromide in carbonyl chloride is exposed to light, or heated at 100—150°, bromine and carbonic oxide are liberated. If, however, boron bromide is heated in sealed tubes at 150° for about 10 hours with half its weight of carbonyl chloride, almost the whole of the carbonyl chloride is decomposed, and the liquid remains colourless provided the temperature has not materially exceeded 150°. The product yields two fractions, 30—40° and 60—70°, containing a liquid which is only slowly attacked by water. If these fractions are added slowly to a solution of sodium thiosulphate cooled to 0°, and the oily liquids that separate are again distilled, they yield respectively carbonyl chlorobromide and carbonic bromide.

*Carbonyl chlorobromide*,  $\text{COClBr}$ , is a colourless liquid which expands rapidly when heated, and boils at 35—37°; sp. gr. at 0° = 1.98; vapour density 4.85 (Cal. 4.98).

*Carbonyl bromide*,  $\text{COBr}_2$ , is a yellowish liquid, expanding rapidly when heated, and boiling at 63—66°; sp. gr. at 0° = 2.48; vapour density 6.60 (Cal. 6.53).

Both liquids are gradually decomposed by water, and when distilled in contact with air they acquire a yellowish colour, owing to the liberation of bromine. When heated in sealed tubes at 100° with mercury, they are completely decomposed in a few hours. Their vapours are very irritating to the eyes and the respiratory organs.

C. H. B.

**Action of Bromine on Ethers in Presence of Sulphur.** By P. GENVRESSE (*Bull. Soc. Chim.*, 1894, [3], **11**, 888—891).—When bromine is added to a mixture of sulphur and ether, a brisk action takes place, ethylic and hydrogen bromides and water being evolved, the last probably from the action of the hydrogen bromide on the ether. The product contains dibromacetaldehyde, identical with that described by Hagemann (*Ber.*, 1870, **3**, 758). The *hydrate* (compare Pinner, *Annalen*, 1874, **173**, 67) forms colourless crystals, and melts at 63°; it is sparingly soluble in water, but freely in alcohol or ether. Its vapour pressure at ordinary temperatures is considerable, so that it readily dissociates in a dry atmosphere under low pressure; it is also decomposed by light. The vapour is irritating to the eyes.

Amylic ether, prepared by Friedel's method of heating the iodide with excess of the alcohol (10 parts) at 200°, is acted on more quickly than ethylic ether. The chief products are amylic bromide and *bromisovaleraldehyde*; the latter boils and decomposes slightly at 105° (25 mm.), and is stated to be identical with that obtained by Étard (*Abstr.*, 1892, 809).

JN. W.

**Active Amylic Ethereal Salts and Ethers.** By PHILIPPE A. GUYE and L. CHAVANNE (*Compt. rend.*, 1895, **120**, 452—454).—The

position of the maximum of  $[\alpha]_D$  in the series of amylic salts of normal acids of the acetic series (this vol., i, 202) does not vary between 20° and 70°. The values are—

<i>t.</i>	Formate.	Acetate.	Propionate.	Butyrate.	Palmitate.
20—22°	+ 2·01	+ 2·53	+ 2·77	+ 2·69	+ 1·45
60—70	+ 1·98	+ 2·51	+ 2·68	+ 2·54	+ 1·16

Ethers derived from active amylic alcohol ( $[\alpha]_D = -4·4$ ) gave the following results.

	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$ .	Product of asymmetry.
Methylic amylic ether.	87·5—88·5°	0·754	+ 0·39	218
Ethylic amylic „	107·5—109	0·759	+ 0·61	332
Propylic amylic „	125·0—127	0·783	+ 0·90	374
Isobutylic amylic „	145·0—147	0·773	+ 0·98	373
Isoamylic amylic „	—	0·774	+ 0·70	351
Cetylic amylic „	—	0·805	+ 0·31	104
Benzyllic amylic „	231·0—232	0·911	+ 1·83	(307)

Even if the isobutyl and isoamyl compounds are left out, the existence of a maximum in both rotatory power and product of asymmetry is obvious.

Ethereal salts of active secondary amylic alcohol prepared by Le Bel gave him the following results, which, however, must be accepted with some reserve.

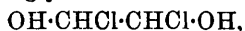
	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$ .	Product of asymmetry.
Secondary amylic acetate. ....	125—130°	0·962	- 4·06	249
„ „ propionate..	145—150	0·895	- 8·55	390
„ „ butyrate....	165—170	0·889	- 8·25	483
„ „ valerate....	—	—	—	490
„ „ caproate ...	—	—	—	487

All the series of compounds investigated show a maximum rotatory power practically coincident with that indicated by the product of asymmetry, but this maximum ought not to occur in all homologous series of active compounds. If in a series of active amylic ethereal salts, the first term should be derived from an acid of high molecular weight, this term will already be on the descending branch of the curve, and the rotatory power will constantly decrease in the series. This is the case with the series of ethereal salts derived from active primary amylic alcohol, the first term being the benzoate.

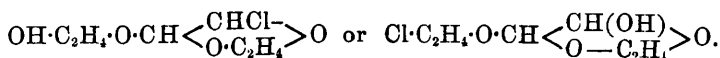
	B. p.	Sp. gr.	Rotatory power $[\alpha]_D$ .	Product of asymmetry.
Amylic benzoate .....	253—254°	0.988	+4.96	275
„ phenylacetate.....	265—266	0.982	+3.84	245
„ phenylpropionate....	279—281	0.976	+2.15	218

C. H. B.

**Action of Chlorine on Ethylenic Glycol.** By LEON DONCIU (*Monatsh.*, 1895, 16, 1—12).—The primary product of the interaction of chlorine and ethylenic glycol is the unstable compound



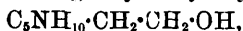
which readily changes into glyoxal. The hydrogen chloride formed during this first change reacts with a further quantity of glycol, producing glycol chlorhydrin, part of which distills over at the temperature of the action, and the remainder combines with more glycol to form polyethylene glycols. By the continued action of chlorine, these are converted into the corresponding aldehydes, and, with them, apparently constitute that portion of the product of the action of chlorine on ethylenic glycol which is insoluble in ether and only sparingly soluble in water. The derivative  $\text{C}_2\text{H}_2(\text{OH})_2\text{Cl}_2$  forms, with 2 mols. of glycol, a compound having the formula  $\text{C}_6\text{H}_{11}\text{ClO}_4$ , and this appears to be the chief part of the product of the action soluble in ether. A substance of the same formula can also be obtained by the interaction of glyoxal, glycol, and chlorhydrin in presence of hydrogen chloride. The compound  $\text{C}_6\text{H}_{11}\text{ClO}_4$  may have the constitution



It is a yellow oil which, on treatment with sodium ethoxide, gives the compound  $\text{C}_2\text{H}_4\left\langle\begin{array}{c}\text{O}\cdot\text{CH}\cdot\text{O} \\ \text{O}\cdot\text{CH}\cdot\text{O}\end{array}\right\rangle\text{C}_2\text{H}_4$ . This melts at 134—135°, and can be synthetically prepared by the interaction of glyoxal and glycol in presence of hydrogen chloride. It appears to bear the same relation to its generators as ordinary acetal does to aldehyde and ethylic alcohol respectively.

G. T. M.

**Ethylenic Oxide.** By ERNST ROITHNER (*Monatsh.*, 1894, 15, 665—682).—The most suitable drying agent for ethylenic oxide is soda-lime, calcium chloride, as employed by Demole (*Annalen*, 173, 125), being decomposed by the moist oxide with formation of lime and ethylene chlorhydrin. When added to a solution of iodine in potassium iodide, ethylenic oxide is converted into iodoform. With piperidine, it forms Ladenburg's hydroxyethylpiperidine,



which yields a hydrochloride melting at 120°. With pyridine, it gives only a resinous mass, but ethylene chlorhydrin and pyridine

yield the expected base, which is characterised by its forming a platinochloride,  $(C_7NH_{10}OCl)_2PtCl_4$ , melting at  $175^\circ$ . When a mixture of ethylenic oxide and phenylhydrazine, in molecular proportion, is heated in sealed tubes at  $100^\circ$ , a product is obtained, the chief portion of which boils at  $180-187^\circ$  (10 mm.), and corresponds nearly with the formula  $N_2H_2Ph \cdot C_2H_4 \cdot OH$ . If, however, a large excess (4-5 mols.) of ethylenic oxide is employed, the oil  $PhN_2H_3 \cdot 5C_2H_4O$  is formed; this boils at  $230-240^\circ$  (10 mm.), and is resolved on treatment with fuming hydrobromic acid into ammonia and ethylenic dibromide. Ethylenic oxide and sodium ethoxide, when heated in sealed tubes at  $100^\circ$ , give a product which boils at  $110-120^\circ$  (25 mm.); this is resolved by hydriodic acid at  $100^\circ$  into ethylic and ethylenic iodides, and must therefore be regarded as a complex ethylic polyethylenic oxide. Ethylenic oxide and phenol, in molecular proportion, when heated in sealed tubes at  $150^\circ$  for 10 hours, yield the *monophenyl derivative of glycol*,  $HO \cdot C_2H_4 \cdot OPh$ ; this boils at  $237^\circ$ , and, when heated with acetic anhydride at  $150^\circ$ , forms a *monacetin*,  $C_{10}H_{12}O_3$ , boiling at  $241-243^\circ$ . If heated with hydrobromic acid or hydriodic acid, the monophenyl derivative is resolved into ethylenic bromide and phenol, and ethylic iodide and phenol respectively.

Ethylenic oxide readily polymerises when it is mixed with a little potash and gently heated at  $50-60^\circ$ . The product melts at  $56^\circ$ , and appears to have a very complex molecule, perhaps  $(C_2H_4O)_{30}$ , since it hardly affects the boiling point and the melting point when it is dissolved in benzene and in acetic acid respectively. It is completely converted into ethylic iodide when heated with hydriodic acid at  $250^\circ$ .

G. T. M.

**Action of Ammonia on *d*-Glucose.** By WINTHROP E. STONE (*Amer. Chem. J.*, 1895, **17**, 191-196; compare Abstr., 1894, i, 221).—*d*-Glucose dissolves in absolute alcohol which has been saturated with ammonia, and the solution is precipitated by carbonic anhydride and by hydrochloric acid, mixtures of glucose and ammonium salts being formed. If the solution is kept in a closed vessel for several weeks, a white, crystalline *ammonia derivative*,  $C_6H_{12}O_6 \cdot NH_3$ , analogous to other aldehyde-ammonias, separates. This compound melts at  $122-123^\circ$  (uncorr.), and has a specific rotation in aqueous solution of  $[\alpha]_D = +22-22.7^\circ$ , no birotation being observed (compare the fact that small quantities of ammonia destroy the birotation observed in sugar solutions). The new ammonia derivative is stable at the ordinary temperature; the presence of the ammonia seems to protect the molecule from many reactions; thus, in solution, the compound is only very slowly fermented by yeast, and with difficulty yields a precipitate with phenylhydrazine; 5.7 milligrams are required in a 1 per cent. solution to reduce 1 c.c. of Fehling's solution (undiluted).

By the action of hydrogen sulphide on the ammoniacal alcohol solution of *d*-glucose, a crystalline compound is obtained which appears to be a thialdine, but has not been thoroughly investigated.

A. G. B.

**Arabinochloral and Xylosochloral.** By MAURICE HANRIOT (*Compt. rend.*, 1895, **120**, 153—155).—Arabinose and xylose do not readily combine with pure chloral, except in presence of a minute quantity of hydrochloric acid. Twenty-five parts of the sugar and 50 parts of anhydrous chloral, with a small quantity of hydrochloric acid, are heated at 100° for an hour, the product repeatedly distilled with water to remove unaltered chloral, and the aqueous solution filtered and concentrated.

Arabinose yields two isomeric substances of the composition  $C_7H_9Cl_3O_5$ , one of which is considerably more soluble in various solvents than the other.  $\beta$ -Arabinochloral forms small crystals or lamellæ, which melt and sublime at 183°. Under reduced pressure, it can be distilled without decomposing. It is only slightly soluble in water and chloroform in the cold, but dissolves somewhat readily in hot alcohol, benzene, or ether. Its rotatory power  $[\alpha]_D = -23.2^\circ$ . With various reagents, it behaves like glucochloral or chloralose (*Abstr.*, 1893, i, 247, and 1894, i, 105), but gives a blue coloration instead of red with a hydrochloric acid solution of orcinol. The triacetyl derivative forms prisms, melts at 92°, and is insoluble in water, but readily soluble in alcohol, ether, and chloroform; it readily decomposes with liberation of acetic acid. Dibenzoylarabinochloral melts at 138°, and is only slightly soluble in ether, although very soluble in alcohol and chloroform. No tribenzoyl derivative is formed, even in presence of zinc chloride. When oxidised with permanganate,  $\beta$ -arabinochloral yields small quantities of an acid which seems to be isomeric with the chloralic acids previously described (*loc. cit.*).

$\alpha$ -Arabinochloral is contained in the mother liquor from the preceding compound, and is more soluble in all solvents; it crystallises in lamellæ which melt at 124°. The dibenzoyl derivative melts at 138°, and is very soluble in ether, alcohol, and chloroform. The acetyl derivative is insoluble in water, but soluble in organic solvents.

Xylosochloral is formed less readily under similar conditions, and requires more hydrochloric acid and longer heating. It crystallises from water in lamellæ which melt at 132°, and sublime partially below this temperature. Its rotatory power  $[\alpha]_D = -13.6^\circ$ , and it gives a blue coloration with orcinol in acid solution; it is much more soluble in water than arabinochloral. The acetyl derivative is unstable, and was not isolated. Dibenzoylxylosochloral forms small crystals insoluble in water.

The constitution of these derivatives is similar to that of glucochloral (*loc. cit.*), and it is probable that the anhydric oxygen is derived from two of the secondary hydroxyl groups, the tertiary hydroxyl remaining unaltered.

C. H. B.

**Acetates derived from Sugars.** By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 194—197).—Experiments were made with a view to determine the influence of the presence of fused sodium acetate and zinc chloride respectively on the acetates obtained by the action of acetic anhydride on sugars. Stable sugars, such as inosite, yield the same products in either case. Saccharoses and polysaccharides in presence of sodium acetate yield salts from which the original carbo-

hydrates can be obtained by the action of alkalis, and the molecular weights of which, as determined by cryometric methods, agree with the formulæ. On the other hand, in presence of very small quantities of zinc chloride, the acetates obtained are those of the glucoses derived from the saccharoses and polysaccharides by hydrolysis.

With glucoses, the reaction is more complex. From ordinary dextrose, three *pentacetins*,  $\alpha$ ,  $\beta$ , and  $\gamma$ , can be obtained under different conditions. The  $\alpha$ -*pentacetin* is obtained when very small quantities of zinc chloride or somewhat larger quantities of sodium acetate are used; it forms silky needles which melt at  $130^\circ$ ; dextrorotatory power in 9 per cent. solution in chloroform or benzene  $[\alpha]_D = +4^\circ$ . At  $15^\circ$ , it dissolves in 76 parts of alcohol of  $95^\circ$ , 47 parts of ether, and 7 of benzene, and is slightly soluble in water, and soluble in all proportions in chloroform. The  $\beta$ -*pentacetin* constitutes about 20 per cent. of the product when a large quantity of sodium acetate is used, and is almost the sole product with a moderate quantity of zinc chloride. It melts at  $82^\circ$ , and its dextrorotatory power in a 9 per cent. solution in chloroform is  $[\alpha]_D = +59^\circ$ . It is more soluble in all the solvents than the  $\alpha$ -derivative. The  $\gamma$ -*pentacetin* is obtained by boiling either of the preceding compounds with 5 per cent. of zinc chloride, and twice their weight of acetic anhydride. It forms needles which melt at  $111^\circ$ ; dextrorotatory power  $[\alpha]_D = +101.75^\circ$ ; solubility in alcohol and ether intermediate between that of the  $\alpha$ - and  $\beta$ -compounds, but extremely soluble in chloroform and benzene. C. H. B.

**Araban.** By F. ULLIK (*Chem. Centr.*, 1894, ii, 31—32; from *Öster. Z. Zucker-Ind. u. Landw.*, 1894, 23, 268—275).—*Araban*,  $C_6H_{12}O_6$ , is a compound which possesses the properties characteristic of an anhydride of arabinose, and has been isolated from the pulp of the sugar-beet and from other beet-root products. It is a white, amorphous substance, insoluble in alcohol, but soluble in water. The aqueous solution does not reduce Fehling's solution, nor does it give precipitates with the hydroxides of the alkali and alkaline earth metals, nor with normal and basic lead acetates; hence the behaviour of the compound resembles that of dextrin. *Araban* shows Tollens' reaction with phloroglucinol and hydrochloric acid, and is optically active,  $[\alpha]_D = -83.9$ ; dilute acids easily convert it into arabinose. Treatment with strong sulphuric acid converts arabinose into a substance which completely resembles *araban* in most of its properties, but has a rotation of  $[\alpha]_D = +242.1$ ; this rotation, however, is dependent on the temperature of treatment, just as, according to Hönig and Schubert, is the case with the rotation of dextrin.

A. G. B.

**Blue Iodine Compounds of Starch and Cholic acid.** By FRITZ W. KÜSTER (*Ber.*, 1895, 28, 783—785; compare this vol., i, 199).—The author insists, in opposition to Mylius (this vol., i, 313), that the blue "compound" of iodine with starch is really a solid solution of iodine in starch; were it a compound, it would give, by dissociation in contact with potassium iodide solution, a solution in which the concentration of the iodine would be constant, whereas, in fact, this concentration alters with that of the solid. Cholic acid,



however, forms a true compound with iodine, for in this case the concentration of the iodine in the contiguous potassium iodine solution is actually constant.

C. F. B.

**Chitin and the Cell Membrane of Fungi.** By EUGEN GILSON (*Ber.*, 1895, 28, 821—822).—The author claims priority over Winterstein (this vol., i, 80) and Hoppe-Seyler (this vol., i, 166) with regard to the discovery of the fact that the characteristic reactions of chitin are also given by the cell-membrane of many species of fungus.

A. H.

**Two Carbohydrates from Fungi.** By ERNST WINTERSTEIN (*Ber.*, 1895, 28, 774—777).—The carbohydrates are extracted from the fungus by digestion with cold 6 per cent. aqueous soda, the proteids having been first removed by treatment with very dilute ammonia; they are then precipitated from the alkaline solution by the addition of acids or salts. Both are white, amorphous substances and greatly resemble the paralextran obtained from *Boletus edulis* (*Abstr.*, 1894, i, 161); they yield *d*-glucose when hydrolysed.

*Paraisodextran*,  $C_6H_{10}O_5$ , from *Polyporus betulinus*, does not reduce Fehling's solution, and is optically active, having a specific rotation  $[\alpha]_D = +240^\circ$  in a 4 per cent. solution in 5 per cent. soda; it is coloured blue by strong sulphuric acid and iodine. *Pachymose* (C 41.07, H 7.07 per cent.), from *Pachyma cocos*, originally prepared by Champignon, is coloured yellow by iodine and sulphuric acid; optical activity could not be detected in it.

C. F. B.

**Action of Nitric acid on Lignocelluloses.** By EDWARD C. C. BALY and JOHN C. CHORLEY (*Ber.*, 1895, 28, 922—927).—The chief object of this investigation was the determination of the gaseous products formed by the oxidation of wood with nitric acid. Box-wood was treated with 33 per cent. of nitric acid (10 per cent. solution), during 4—5 hours, and the action completed by heating on the water bath. In one experiment, 9 grams of wood, dried at  $100^\circ$ , and 35 grams of nitric acid (9.64 per cent.) yielded 1156 c.c. of gas consisting of  $N_2 = 18.3$ ;  $N_2O = 9.4$ ;  $NO = 9.3$ ;  $NO_2 = 33.2$ ;  $HCN = 8.3$ ;  $CO_2 = 17.2$ ;  $CO = 4.3$  per cent. This shows that the amount of nitric acid completely reduced, to  $N_2$  or  $N_2O$ , corresponds with only 20 per cent. of the wood employed, and that only 2.95 per cent. of the carbon of the wood is converted into gaseous substances. The remaining products of the oxidation consisted of: fibrous residue = 48.00; volatile acids = 11.80; oxalic acid = 3.84; soluble derivatives of the non-celluloses = 26.16 per cent. The fibrous residue was almost pure cellulose; the volatile acids are calculated as acetic acid, and consisted chiefly of this; the proportion varies according to the material employed, with jute it is similar to box-wood, with pine only 3—4 per cent. is formed. The soluble substances are strongly acid, and no definite compound could be isolated. When further oxidised, oxalic acid, oxides of carbon, and volatile acids are formed; when fused with alkali, carbonic anhydride, oxalic acid, and acetic acid are produced. The reaction consists essentially in the destructive oxidation of a keto-R-hexene

group of the "non-cellulose" complex, whilst the pentosans, which are simultaneously formed, dissolve.

J. B. T.

**Isoundecylamine.** By GIACOMO PONZIO (*Gazzetta*, 1894, **24**, ii, 277—288).—*Isoundecylamine*,  $\text{NH}_2\cdot\text{CHMe}\cdot\text{C}_9\text{H}_{19}$ , prepared by reducing methylonylketoxime with sodium amalgam in acetic acid solution, is a colourless, hygroscopic liquid, lighter than and insoluble in water; it boils at  $230\text{--}231^\circ$  under 741 mm. pressure, has an alkaline reaction, readily absorbs carbonic anhydride, and soon changes to a white, solid mass on exposure to air. Its *hydrochloride*,  $\text{C}_{11}\text{H}_{23}\cdot\text{NH}_2\cdot\text{HCl}$ , which crystallises in flat needles melting at  $83\text{--}84^\circ$ , is soluble in ether or light petroleum, and, with mercuric chloride, forms a white compound,  $(\text{C}_{11}\text{H}_{23}\text{N}\cdot\text{HCl})_2\text{HgCl}_2$ ?, soluble in alcohol. The *platinochloride* crystallises in lustrous, yellow laminæ which blacken at  $240^\circ$ . The *acetyl*,  $\text{C}_{11}\text{H}_{23}\cdot\text{NHAc}$ , and *benzoyl*,  $\text{C}_{11}\text{H}_{23}\cdot\text{NHBz}$ , derivatives, prepared in the ordinary way, crystallise in thin needles melting at  $58^\circ$  and  $84^\circ$  respectively. The *benzylidene* derivative,  $\text{C}_{11}\text{H}_{23}\cdot\text{N}:\text{CHPh}$ , is prepared by the aid of benzaldehyde; it is a colourless liquid, boiling at  $197\text{--}198^\circ$  under 17 mm. pressure, but decomposing at  $240^\circ$  under atmospheric pressure.

*Isoundecylammonium isoundecyldithiocarbamate*,



prepared by the action of carbon bisulphide on isoundecylamine in ethereal solution, crystallises in small, white prisms melting at  $66^\circ$ . On heating with alcohol, it yields  $\alpha$ -*diisoundecylthiocarbamide*,  $\text{CS}(\text{NH}\cdot\text{C}_{11}\text{H}_{23})_2$ , which crystallises in lustrous laminæ melting at  $50\text{--}51^\circ$ ; on treating this with potassium platinochloride in alcoholic solution, *platodisoundecylthiocarbamide*,  $4\text{CS}(\text{NH}\cdot\text{C}_{11}\text{H}_{23})_2\cdot\text{PtCl}_2$ , is obtained as a yellow powder melting at  $60^\circ$ .

$\alpha$ -*Diisoundecylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_{11}\text{H}_{23})_2$ , is obtained by the action of yellow mercuric oxide on the corresponding thio-compound; it crystallises in lustrous, flat needles melting at  $94\text{--}95^\circ$ .

*Isoundecylthiocarbimide*,  $\text{C}_{11}\text{H}_{23}\cdot\text{N}:\text{CS}$ , is obtained together with isoundecylamine hydrochloride by distilling isoundecylammonium isoundecyldithiocarbamate with mercuric chloride and water; it is a colourless liquid, possessing but a slight odour of mustard oil, and boils at  $163\text{--}164^\circ$  under 17 mm. pressure, but decomposes slightly at  $270^\circ$  under atmospheric pressure. On treatment with alcoholic ammonia, it yields *monisoundecylthiocarbamide*,  $\text{C}_{11}\text{H}_{23}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , which crystallises in lustrous tablets melting at  $95^\circ$ ; the *platoso-*derivative is obtained in yellow crusts melting at  $200^\circ$ .

*Monisoundecylcarbamide*,  $\text{C}_{11}\text{H}_{23}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the action of yellow mercuric oxide on the corresponding thio-compound, crystallises in lustrous laminæ melting at  $127^\circ$ .

*Isoundecylphenylthiosemicarbazide*,  $\text{C}_{11}\text{H}_{23}\cdot\text{NH}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{NHPh}$ , is obtained in two stereoisomeric forms by the action of phenylhydrazine on isoundecylthiocarbamide; the  $\alpha$ - or labile modification melts at  $80\text{--}100^\circ$ , and changes on heating into the stable  $\beta$ -form, which crystallises in lustrous laminæ melting sharply at  $109^\circ$ .

W. J. P.

**Action of Formaldehyde on Hydroxylamine and Methylamine Hydrochlorides.** By ANDRÉ BROCHET and R. CAMBIER (*Compt. rend.*, 1895, **120**, 449—452).—When excess of formaldehyde is added to a solution of hydroxylamine hydrochloride, the whole of the hydrochloric acid is liberated; if, on the other hand, the hydrochloride is in excess, the quantity of acid liberated is strictly proportional to the quantity of aldehyde added, and, by titrating with methyl-orange as indicator, the aldehyde can then be accurately estimated.

If a solution containing formaldehyde and any salt of hydroxylamine, whether acid or alkaline, is boiled, hydrocyanic acid is formed, and this is a delicate and characteristic reaction for formaldehyde, since other aldehydes yield nitriles.

When formaldehyde and methylamine hydrochloride are mixed in solution, the liquid remains neutral to methyl-orange, and becomes acid to phenolphthalein, owing to the formation of a weak base, which separates as an upper layer on adding excess of solid potash. This base, which boils at  $166^{\circ}$ , was first obtained by L. Henry (*Bull. Acad. Sci. Belge*, [3], **26**, 200), who found its vapour density to be 1.52, and regarded it as the compound  $\text{NMe}:\text{CH}_2$ . It seemed unlikely, however, that a compound of this constitution should boil at so high a temperature, and the authors find that it is really trimethyltrimethylenetriamine, its vapour density being 1.81 (Cal. 1.49), and its molecular weight by the cryometric method in benzene 122.75 (Cal. 129). It yields very soluble salts, which do not crystallise from water or alcohol, but the hydrochloride can be obtained in crystals by the action of dry hydrogen chloride on a solution of the base in benzene.

C. H. B.

**Action of Formaldehyde on Methylamine and Ammonia.** By PAUL DUDEN and MAX SCHARFF (*Ber.*, 1895, **28**, 936—939).—The mechanism of the formation of hexamethylenetetramine has not yet been ascertained, although in all probability a simple condensation occurs in the first instance similar to that which takes place between formaldehyde and the primary amines. The relatively stable, feeble bases thus formed, of which methylenemethylamine is a type, are considered by L. Henry to be represented by the formula  $\text{CH}_2:\text{NR}$ , but Brochet and Cambier (preceding abstract), from observations of vapour density, find that this formula must be tripled, a view confirmed by v. Miller and Plöchl's investigation of anhydroformaldehydeaniline, which undoubtedly has the formula  $(\text{CH}_2:\text{NPh})_3$ .

To decide the question of the molecular weight of methylenemethylamine from a purely chemical standpoint, the authors have prepared the picrate, and find that its formula is  $(\text{CH}_2:\text{NMe})_3, \text{C}_6\text{H}_5\text{N}_3\text{O}_7$ , thus confirming Brochet and Cambier's conclusions. Trimethyltrimethylenetriamine picrate, from the perfectly dry base and acid in ethereal solution, crystallises in large prisms, and melts at  $127$ — $128^{\circ}$ ; it is soluble in water, by which it is hydrolysed, on boiling, into formaldehyde and methylamine picrate.

Attempts to prepare a similar picrate from the product of the action of formaldehyde on aqueous ammonia were unsuccessful, nor

could a definite platinochloride or aurochloride be obtained. On adding benzoic chloride, however, to the product in presence of excess of caustic soda, *tribenzoyltrimethylenetriamine*,  $(\text{CH}_2\cdot\text{NBz})_3$ , was obtained as a sticky, curdy mass, which, after purification, crystallised from ether-chloroform in small, well-defined, colourless octahedra, and melted at  $220\text{--}221^\circ$ ; its molecular weight was determined by the cryoscopic method. It was accompanied by a small quantity of a substance melting at  $202\text{--}204^\circ$ . Tribenzoyltrimethylenetriamine is hydrolysed by mineral acids into benzoic acid, formaldehyde, and ammonia, but although in this respect as well as in melting point it resembles methylenedibenzamide (*Annalen*, 1884, **223**, 47), it is not identical with that substance, as its crystallographic constants and solubilities are quite different.

The authors consider that the probable constitution of these methyleneamines is  $\text{NR} < \begin{smallmatrix} \text{CH}_2\cdot\text{NR} \\ \text{CH}_2\cdot\text{NR} \end{smallmatrix} > \text{CH}_2$ .

J. N. W.

**Action of Formaldehyde on Ammonium Salts.** By ANDRÉ BROCHET and R. CAMBIER (*Compt. rend.*, 1895, **120**, 557—560).—When formaldehyde is mixed with ammonium chloride, trimethylenetriamine hydrochloride is probably formed (this vol., i, 325) with liberation of hydrochloric acid, but the latter tends to reverse the action, and hence a condition of equilibrium is set up varying with the temperature, &c. If the acid is neutralised, by means of chalk or otherwise, as fast as it is formed, hexamethylenetetramine is obtained, but, if the proportion of acid is increased sufficiently, the products are completely reconverted into ammonium chloride and formaldehyde. It would seem that one or more bases exist intermediate between ammonium and hexamethylenetetramine. The proportion of nitrogen in the platinochlorides obtained from the solution increases with the proportion of hydrochloric acid present, and nitrous acid yields nitroso-derivatives of pentamethylenetetramine and trimethylenetriamine.

If a solution of formaldehyde and ammonium chloride is heated, the former, whether present in excess or not, acts on the trimethylenetriamine first formed, and yields methylamine in calculated quantity,  $2(\text{CHNH}_2\text{Cl})_3 + 3\text{CH}_2\text{O} + 3\text{H}_2\text{O} = 6\text{NH}_2\text{Me}\cdot\text{HCl} + 3\text{CO}_2$  (compare Delépine, following abstract). If the ammonium chloride is in large excess, the amine is very pure; if the aldehyde is in large excess, trimethylamine is the final product.

The formation of trimethylamine from ammonium salts and excess of formaldehyde has been observed by Plöchl (*Abstr.*, 1888, 1051). Other ammonium salts behave similarly, hexamethylenetetramine being the sole product if the liquid is kept neutral. In hot solutions, methylamines are formed together with some methylal produced by the action of the aldehyde on the methylic alcohol, which is usually present as an impurity.

C. H. B.

**Hexamethylenetetramine.** By MARCEL DELÉPINE (*Compt. rend.*, 1895, **120**, 197—199; 501—502).—Hexamethylenetetramine can be obtained by the action of a solution of ammonia in methylic alcohol

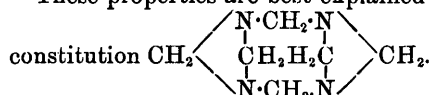
on methylenic chloride and chlorobromide. Cryometric determinations in acetic acid solution freshly prepared indicate a molecular weight of 137 (Cal. 140), but the value decreases with the time, in consequence of partial decomposition of the amine, which can be readily detected by means of Nessler's reagent, on which the amine itself has no action. The platinochloride has the composition  $C_6H_{12}N_4, H_2PtCl_6 + 4H_2O$ .

Inorganic acids convert the amine into ammonia and the aldehyde. Methylic and ethylic iodides yield derivatives of the type  $C_6H_{12}N_4RI$ , as Vohle has stated, and the author finds that they have the properties of quaternary ammonium iodides, and hence hexamethylenetetramine is a tertiary base.

Griess described a nitroso-derivative, dinitrosopentamethylenetetramine,  $(CH_2)_5(NO)_2N_4$ , which yields nitrogen, ammonia, and formaldehyde when heated with dilute hydrochloric acid. With cold acetic acid, however, the reaction is  $2(CH_2)_5(NO)_2N_4 = (CH_2)_6N_4 + 4N_2 + 4CH_2O$ , the same quantity of nitrogen being liberated, but the residues  $(CH_2)_3N_2$  combining to form the original amine instead of undergoing hydrolysis. Mayer described another nitroso-derivative,  $(CH_2 \cdot N \cdot NO)_n$ , and he adopted 3 as the value of  $n$ . The author, however, considers that the compound is  $(CH_2)_4(NO)_4N_4$ , and, as a matter of fact, the compound has no basic properties, whereas Griess's compound is dibasic.

With nascent hydrogen, hexamethylenetetramine yields trimethylamine and ammonia.

These properties are best explained by ascribing to the amine the



*Hexamethylenetetramine amyliodide* forms white, nacreous lamellæ, which soften at  $146^\circ$ , and melt at about  $156^\circ$ ; it combines with three atomic proportions of iodine to form a deep green, crystalline compound, which melts at  $127^\circ$ .

When the hexamethylenetetramine alkyl iodides are boiled with dilute hydrochloric acid, they are hydrolysed in accordance with the equation  $C_6H_{12}N_4RI + 6H_2O = 6CH_2O + 3NH_3 + NRH_3I$ . This reaction affords a new method for the preparation of primary amines. Bismuth iodide is a valuable reagent for the separation of the amines from ammonia, and in the case of amylamine it indicates the presence of a secondary product which is at present under investigation.

C. H. B.

**Triacetoneamine.** By ICLIO GUARESCHI (*Chem. Centr.*, 1894, ii, 197—198; from *Atti. Accad. Sci. Torino*, 29).—Mesityl oxide is converted into diacetoneamine by the action of ammonia, similarly *triacetoneamine* is produced by the action of ammonia on phorone, even in the cold. It forms large, colourless crystals melting at  $34.9^\circ$ , when moist at  $39.6^\circ$ ; the *platinochloride*,  $(C_9H_{17}NO)_3, H_2PtCl_6$ , may be crystallised with  $3H_2O$ ; the *platinothiocyanate* is a lemon-yellow salt. By employing amines instead of ammonia in the above reaction, alkyl derivatives of triacetoneamine are obtained. *Methyltriacetoneamine*,

$C_9H_{16}MeNO$ , is a yellow, alkaline oil of unpleasant odour, forming a crystalline *platinochloride*, *platinothiocyante*, *chloride*, *aurochloride*, and *picrate*. *Ethyltriacetonamine* is also a yellowish, strongly-alkaline oil, from which many salts have been prepared. *Allyltriacetonamine*,  $C_3H_5 \cdot C_9H_{16}NO$ , cannot be obtained quite pure, as it is readily resolved into allylamine and phorone, but the author obtained a crystalline *platinochloride*.

In the reaction with benzylamine and phorone, another base is produced as well as *benzyltriacetonamine*,  $C_9H_{16}(C_7H_7)NO$ ; the former will be described in a future communication, the latter is a colourless, alkaline liquid, resembling in odour triacetoneamine and trimethylamine; it cannot be crystallised, but has yielded many salts.

D. A. L.

#### Action of Ethylenediamine on Phorone and Mesityl Oxide.

By ICILIO GUARESCHI (*Chem. Centr.*, 1894, ii, 198; from *Atti Accad. Sci. Torino*, 29).—Pulverised phorone, mixed with ethylenediamine hydrate dissolved in water, yields acetone and a base,  $C_8H_{16}N_2$ , which has not been named, but is also produced by the action of ethylenediamine on mesityl oxide. It is an oily liquid with pungent odour, and appears to crystallise after prolonged exposure over sulphuric acid; the *platinochloride*,  $C_8H_{16}N_2 \cdot H_2PtCl_6$ , and the *platinothiocyante* have been prepared. It decomposes into ethylenediamine and acetone when distilled with water.

D. A. L.

#### Action of Nitrous acid on Amidouracil and Amidoacetone.

By ANGELO ANGELI (*Gazzetta*, 1894, 24, ii, 366—371).—The author has previously suggested (*Gazzetta*, 23, ii, 442) that the peculiar behaviour of the amidogen group in amidomethyluracil is due to the presence of the group  $\cdot CO \cdot \overset{|}{C} \cdot NH_2$ ; it is now shown that amidouracil itself can be converted into the diazo-compound which Behrend and Ernert (*Abstr.*, 1890, 1240) prepared from amidouracilcarboxylic acid.

Amidoacetone also yields a *diazo-compound*; it was, however, only obtained in an impure state as a yellow oil, which effervesces with hydrochloric acid and yields bromacetone with hydrobromic acid. It is probably diazoacetylmethane,  $CHAc < \overset{N}{\underset{N}{|}}{C}$ . No diazo-compound could be prepared from diamidoacetone.

W. J. P.

#### Diazomethane.

By HANS v. PECHMANN (*Ber.*, 1895, 28, 855—861; compare *Abstr.*, 1894, i, 438).—Diazomethane may be prepared by the action of aqueous or alcoholic alkalis on nitroso-acidyl derivatives of methylamine, especially on nitrosomethylurethane. This compound is best prepared by leading nitrous gases into urethane diluted with its own volume of ether. It is dangerous on account of its powerfully irritating action on the skin, lungs, and eyes; in these properties it resembles diazomethane. To prepare diazomethane, 1—5 c.c. of the above compound is mixed with an excess of dry ether and heated with excess of potash dissolved in methylic alcohol. About 50 per cent. of the theoretical yield of diazomethane is found

in the distillate. At ordinary temperatures it is a gas, but may be condensed to a dark yellow liquid, which boils at about  $0^{\circ}$ . Both organic and inorganic acids are converted into their methylic salts when treated with diazomethane in the cold. Alcohol is not acted on at ordinary temperatures, but phenol is slowly converted into anisole, and picric acid into trinitroanisole. Bases react with diazomethane just as they do with ethylic diazoacetate; thus, paratoluidine gives methylparatoluidine.

The author suggests the use of diazomethane as a reagent for the preparation of the methylic derivatives of acids, phenols, and similar compounds in those cases in which the methylic derivatives cannot be readily obtained by other methods. As examples are given dimethylic phenylhydrazonemesoxalate, methylphthalimide, and  $\beta$ -methylumbelliferone methylic ether. When diazomethane is reduced with sodium amalgam and alcohol, the main product is methylhydrazine.

Diazomethane reacts with quinone, nitrosophenol, and nitroso-methylaniline, forming yellow or red compounds, which are being subjected to further examination. It also, like ethylic diazoacetate, unites with many unsaturated compounds to form additive compounds, but others, for instance, ethylene, stilbene, acetylene, toluene, &c., are not acted on.

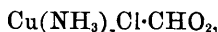
J. J. S.

**Elimination of Carbonic Oxide.** By WILHELM WISLICENUS (*Ber.*, 1895, **28**, 811—814; compare *Abstr.*, 1894, i, 323).—Elimination of carbonic oxide on heating only occurs quantitatively in the case of derivatives of ethylic oxalacetate which contain the group  $\text{COOEt}\cdot\text{CO}\cdot\text{CH}\cdot\text{COOEt}$ , but the action does take place, more or less completely, with a very large number of ketonic substances, among which are ethylic phenylecyanopyruvate, ethylic acetophenoneoxalate, from which ethylic benzoylacetate may be thus advantageously prepared, acetophenoneoxalic acid, ethylic ketipate, oxalyldiacetone, oxalyldiacetophenone, and diphenylketipionitrile.

The sodium and copper compounds of the ethereal oxalacetates either do not decompose at all, or only very slowly, even at temperatures above  $200^{\circ}$ .

A. H.

**Cuprammonium Double Salts.** By THEODORE W. RICHARDS and ANDREW H. WHITRIDGE (*Amer. Chem. J.*, 1895, **17**, 145—154; compare *Abstr.*, 1894, i, 113).—*Cuprammonium formochloride*,



is prepared by dissolving cupric formate in alcohol, adding ammonium chloride, and passing ammonia into the liquid until a slight excess is present. The salt separates in blue, prismatic crystals on evaporation.

*Ammoniocuprammonium acetobromide*,  $\text{Cu}(\text{NH}_3)_3\text{Br}\cdot\text{OAc} + \text{H}_2\text{O}$ , is prepared like the ammoniocuprammonium acetochloride (*Abstr.*, 1894, i, 113), which it resembles, except that it is much less stable.

*Cuprammonium propionobromide*,  $\text{Cu}(\text{NH}_3)_2\text{Br}\cdot\text{C}_3\text{H}_5\text{O}_2$ , was prepared by dissolving ammonium propionate in absolute alcohol, passing dry ammonia into the solution, and then warming it with precipitated

cupric oxide; very blue, prismatic crystals were deposited on evaporation.

*Cuprammonium lactobromide*,  $\text{Cu}(\text{NH}_3)_2\text{Br}\cdot\text{C}_3\text{H}_5\text{O}_3$ , is formed when syrupy lactic acid and cupric bromide are dissolved in alcohol and the solution is saturated with ammonia. It forms light blue crystals, which have a faint tinge of purple, and are permanent in air but immediately decomposed by water.

*Cuprammonium lactochloride*,  $\text{Cu}(\text{NH}_3)_2\text{Cl}\cdot\text{C}_3\text{H}_5\text{O}_3$ , resembles the bromide, but is of lighter colour; it is similarly prepared.

Similar compounds containing butyric acid could not be obtained.

A. G. B.

**Cuprammonium Double Salts.** By THEODORE W. RICHARDS and GEORGE OENSLAGER (*Amer. Chem. J.*, 1895, **17**, 297—305; compare Abstr., 1894, i, 113).—Attempts to prepare cuprammonium-acetofluoride proved fruitless. The following new iodine compounds have been prepared and analysed.

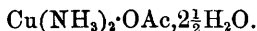
1. *Ammoniocuprammonium acetoiodide*,  $\text{Cu}(\text{NH}_3)_3\text{I}\cdot\text{OAc}$ , which forms brilliant, deep blue, monoclinic plates. It is not very permanent in the air, and is at once decomposed by water and acids.

2. *Octocuprammonium iodide acetate*,  $\text{Cu}_8(\text{NH}_3)_{16}\text{I}(\text{OAc})_{15}$ , large, deep blue crystals, obtained from the mother liquors of the above compound.

3. *Tetrammoniotricuprammonium iodide*,  $\text{Cu}_3\text{I}_6(\text{NH}_3)_{10}$ . The crystals are black, and possess a bronze lustre, which soon disappears. They are immediately decomposed by water.

4. *Ammonium dicupric acetate*,  $\text{NH}_4\text{Cu}_2(\text{OAc})_3 + \text{H}_2\text{O}$ . This forms bluish-green crystals, which dissolve in water without undergoing decomposition.

5. Cuprammonium acetate,  $\text{Cu}(\text{NH}_3)_2\cdot\text{OAc}$ , and also



These two compounds have been previously obtained by F. Foerster (Abstr., 1893, i, 131). These, and other compounds, are being further investigated. J. J. S.

**Action of Ethylic  $\alpha$ -Bromopropionate on Alkali Nitrites.** By GASTON LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], **11**, 886—888; compare Abstr., 1894, i, 114, and this vol., i, 169).—In preparing the nitrosopropionates by this method, 2 mols. of sodium nitrite are necessary; probably the nitro-compound is formed in the first instance, and subsequently reduced by a second molecule of the nitrite. In confirmation of this view, when potassium nitrite is substituted for the sodium salt, potassium nitrate may be separated from the product.

An oily bye-product,  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_7$ , obtained in preparing ethylic nitrosopropionate, was probably *ethylic dinitrosolactate*, corresponding with the methylic salt previously described. J. N. W.

**Alkyl Nitrosobutyrate.** By GASTON LEPERCQ (*Bull. Soc. Chim.*, 1894, [3], **11**, 883—886).—*Methylic  $\alpha$ -nitrosobutyrate* forms a



brilliant, white mass, and melts at  $61^{\circ}$ . Like the nitrosopropionate, it is easily soluble in dilute alkalis, so that the molecule probably contains a  $\text{C:NOH}$  group. The silver salt was prepared. The ethylic salt resembles the methylic salt, and melts at  $51^{\circ}$ .

On attempting to prepare ethylic nitrosoisobutyrate, the nitroso-propionate was obtained. J. N. W.

**Daturic acid.** By ERNEST GÉRARD (*Compt. rend.*, 1895, **120**, 565—567).—A summary of those properties of daturic acid and its derivatives (Abstr., 1890, 1395, and 1892, 582), which prove that this acid is a distinct chemical individual and not a mixture of palmitic and stearic acids. C. H. B.

**Substituted Ethereal Salts of Glycollic acid (Glycolylhydrazine).** By THEODOR CURTIUS and NICOLAUS SCHWAN (*J. pr. Chem.*, 1895, [2], **51**, 353—371).—Ethylic glycollate may be prepared by adding the calculated quantity of water to a solution of ethylic diazoacetate (30 grams) in ether (100 grams), and dropping in 2 drops of sulphuric acid (1 : 5), the liquid being rapidly stirred the while. When the evolution of nitrogen has subsided, 4 grams of water and 14 drops of the acid are gradually added, excess of water is removed by calcium chloride, and the ethereal solution fractionated.

*Ethylic benzylglycollate*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOEt}$ , is obtained when ethylic diazoacetate (5 grams) and benzylic alcohol (4.75 grams) are heated together until the evolution of nitrogen has ceased; it distils at  $153\text{--}154^{\circ}$  (12 mm.), and is a clear, colourless liquid, which becomes yellow after a time.

It was found that pure ethylic diazoacetate cannot be made to react with absolute alcohol, notwithstanding that the impure salt forms ethylic ethylglycollate under these conditions (compare *J. pr. Chem.*, 1888, [2], **38**, 424). Ethylic benzoylglycollate has been described before (*loc. cit.*). Ethylic hippurylglycollate (*loc. cit.*) may be prepared from ethylic diazoacetate and hippuric acid; the corresponding acid appears to be very unstable, attempts to hydrolyse the ethylic salt resulting in the production of ethylic hippurate.

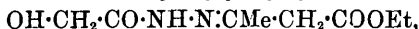
*Ethylic oxalylglycollate*,  $\text{C}_2\text{O}_2(\text{O}\cdot\text{CH}_2\cdot\text{COOEt})_2$ , is prepared by gradually adding 3.15 grams of anhydrous oxalic acid to 8 grams of ethylic diazoacetate, care being taken that the temperature does not rise; 2—4 grams of ethylic diazoacetate are next added, and when no more nitrogen is evolved the vessel is warmed until the liquid becomes clear; the crystals which separate on cooling are washed with ether, dissolved in that menstruum, the solution washed with alkali, dried by calcium chloride, and evaporated. Ethylic oxalylglycollate crystallises in slender, white needles, softens at  $54^{\circ}$ , melts at  $58^{\circ}$ , and dissolves sparingly in cold ether, more freely in alcohol, but not in water. *Ethylic succinylglycollate*,  $\text{C}_2\text{H}_4(\text{COO}\cdot\text{CH}_2\cdot\text{COOEt})_2$ , is prepared in a similar manner; it forms long, colourless needles or laminæ, melts at  $72.5^{\circ}$ , and dissolves in hot ether and alcohol.

Hydrazine hydrate reacts with ethylic hippurylglycollate to form hippurylhydrazine (Abstr., 1891, 56) and glycolylhydrazine; with ethylic oxalylglycollate to form oxalylhydrazine (this vol., i, 264) and

glycolylhydrazine; and with ethylic succinylglycollate to form succinylhydrazine (*loc. cit.*) and glycolylhydrazine. Ethylic benzylglycollate and hydrazine hydrate react to form *benzylglycolylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , which yields *benzylidenebenzylglycolylhydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$ , when shaken with benzaldehyde; the last-named compound melts at  $95^\circ$ , and is freely soluble in hot, absolute alcohol.

The properties of *glycolylhydrazine*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , have been already described as those of amidoglycocine (hydrazineacetic acid, Abstr., 1891, 56). The compound is best prepared from ethylic oxalylglycollate, as indicated above, the oxalylhydrazine crystallising first; it yields the *hydrochlorides*,  $\text{C}_2\text{H}_6\text{O}_2\text{N}_2\cdot\text{HCl}$  (in aqueous solution), and  $\text{C}_2\text{H}_6\text{O}_2\text{N}_2\cdot 2\text{HCl}$  (in alcoholic solution); the latter melts at  $145\text{--}160^\circ$ . With sodium ethoxide, it yields the compound  $\text{C}_2\text{H}_6\text{O}_2\text{N}_2 + \text{EtONa}$ .

*Benzylideneglycolylhydrazine* has been described as benzylidenehydrazineacetic acid (*loc. cit.*). *Orthohydroxybenzylideneglycolylhydrazine*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , crystallises in yellowish-white, felted needles, and melts at  $220\text{--}221^\circ$ ; the *para*-compound melts at  $215\text{--}216^\circ$ . *Acetophenoneglycolylhydrazine*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMePh}$ , obtained by heating acetophenone with the hydrazine at  $130^\circ$ , forms yellowish-white needles. *Ethylic glycolylhydrazineacetate*,



forms bitter crystals, melts at  $112^\circ$ , and dissolves freely in absolute alcohol, benzene, and ether.

*Glycolylhydrazine anhydride (hydraziglycolide)*,  $\begin{array}{c} \text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2 \end{array}$ , is obtained when glycolylhydrazine is heated for 10 hours in an oil bath at  $170\text{--}175^\circ$ , and the product recrystallised from alcohol; it crystallises in slender needles or laminae, melts at  $205\text{--}206^\circ$ , and dissolves easily in water at  $20^\circ$ , but hardly at all in water at  $0^\circ$ ; hot alcohol dissolves it, but not ether or benzene. It is decomposed when sublimed; its aqueous solution is neutral, and it behaves as a feeble base dissolving in acids. Caustic alkalis also dissolve it. It is stable towards hot dilute acids and alkalis, and exhibits indifference towards mercuric and silver salts. Its *hydrochloride*,  $\text{C}_2\text{H}_6\text{O}_2\text{N}_4\cdot\text{HCl} + \text{H}_2\text{O}$ , melts at  $40\text{--}42^\circ$ , and is very soluble in water. The formation of this basic anhydride shows that the parent substance is glycolylhydrazine, and not hydrazineacetic acid, as formerly supposed (*loc. cit.*); another argument for the present view is, that when hydrogen chloride is passed into the hot alcoholic solution of glycolylhydrazine no etherification occurs, as would inevitably be the case were the compound hydrazineacetic acid. A. G. B.

**Methylenic Lactate.** By LOUIS HENRY (*Compt. rend.*, 1895, 120, 333—335).—When a mixture of paraformaldehyde with lactic acid in molecular proportion is heated for some time, it yields methylenic lactate,  $\text{CH}_2\cdot\begin{array}{c} \text{O}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CHMe} \end{array}$ , a colourless, mobile liquid, with a strong odour, and an extremely piquant taste. It boils at  $153\text{--}154^\circ$  under a

pressure of 754 mm.; sp. gr. at 25 = 1.1974; vapour density 5.47 (Cal. 3.52); it solidifies in a mixture of ether and solid carbonic anhydride, and melts at  $-28^{\circ}$ . It is insoluble in water, and when heated with it yields lactic acid and formaldehyde, and the liquid has a strong reducing action on silver nitrate. Bromine dissolves it without appreciable effect; it combines explosively with the corresponding propylene derivative, and ammonia and primary and secondary alkylamines decompose it rapidly.

Trioxymethylene and glycerol, or its monochlorhydrin, yield respectively the compounds  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{O}$   
 $\text{CH}_2\cdot\text{O} > \text{CH}_2$ , boiling at  $197^{\circ}$ , and

$\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{O}$   
 $\text{CH}_2\cdot\text{O} > \text{CH}_2$ , boiling at  $150^{\circ}$ .

C. H. B.

**Rotatory Powers of Amylic Pyruvate and Lactate.** By LOUIS SIMON (*Bull. Soc. Chim.*, 1894, [3], 11, 760—767).—*Active amylic pyruvate*, prepared by the direct action of the acid on the alcohol, is a limpid, colourless liquid, having a pleasant but peculiar odour. It boils at  $185\text{--}186^{\circ}$ , or at  $85\text{--}86^{\circ}$  (16 mm.). The sp. gr. = 0.984 at  $15^{\circ}$ . The specific rotatory power,  $[\alpha]_D = +3.25^{\circ}$  at  $15^{\circ}$ , and is practically the same in acetic acid solution, but rather lower ( $+3.12^{\circ}$  to  $+3.21^{\circ}$ ) in ethylic acetate solution. The refractive index,  $[\mu]_D = 1.420617$  at  $19^{\circ}$ ,  $[\mu]_{\infty} = 1.409170$ ; the temperature coefficient =  $-0.000474$ ; the molecular refraction = 65.73, the calculated number being 66.23. *Active amylic lactate*, prepared in the same way from the active alcohol ( $[\alpha]_D = -4.15^{\circ}$ ) and inactive lactic acid, could not be separated into two optical isomerides, the acid obtained by hydrolysis of various portions being invariably inactive. It boils at about  $195^{\circ}$ , or at  $94\text{--}95^{\circ}$  (14 mm.), or  $92^{\circ}$  (11 mm.). The specific rotatory power,  $[\alpha]_D = +2.5^{\circ}$ .

The relation between the specific rotatory powers of these salts is directly opposed to that required by GUYE's law. As a similar deviation is shown by the similarly related compounds, *d*-fructose, *d*-mannose, and *d*-mannitol, it must be assumed that the moment of a ketonic or aldehydic chain is greater than that of the corresponding alcoholic chain.

JN. W.

**Optical Isomerides of  $\alpha$ -Hydroxybutyric acid.** By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1895, 120, 562—565).—Quinine, strychnine, and brucine  $\alpha$ -hydroxybutyrates crystallise well, but the cinchonine salt does not crystallise readily. By fractional crystallisation of these salts, the acid can be separated into its optically isomeric constituents, the best results being obtained with the brucine compound. The salt of the *laevogyrate* acid is less soluble than that of the *dextrogyrate*; after separation of the crystals, they are decomposed with ammonia. The first fractions are *laevogyrate*, but the rotatory power of successive fractions diminishes, and after a time the sign of rotation changes. The specific rotatory power of *laevogyrate* ammonium  $\alpha$ -hydroxybutyrate  $[\alpha]_D = -13.9$ ; for the *isobutylic*  $\alpha$ -hydroxybutyrate  $[\alpha]_D = -7.7$ . This ethereal salt

boils at 190—200°; sp. gr. at 15° = 0.919. The ethereal salts of the lævogryate acid are also lævogryate, and are under investigation.

C. H. B.

**Behaviour of Calcium Ethylglycollate on Dry Distillation.**

By WILHELM H. GINTL (*Monatsh.*, 1894, **15**, 803—806).—On dry distillation, calcium ethylglycollate (compare Heintz, *Jahresber.*, 1861, 448) yields a mixture of alcohol and diethoxyacetone,  $\text{CO}(\text{CH}_2\cdot\text{OEt})_2$ ; the latter boils at 189—194°, is soluble in water, and has a sweet but burning taste. In its mode of decomposition, the salt therefore behaves differently from the calcium salts of alkyl derivatives of hydroxybenzoic acid (compare Hübner, this vol., i, 366).

G. T. M.

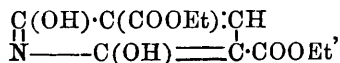
**Condensation of Ethylic Malonate with Acetone.** By ALEXANDER MEYENBERG (*Ber.*, 1895, **28**, 785—787).—Ethylic malonate (1 mol.) and acetone (1 mol.), when heated for 14 hours at 100° with acetic anhydride (1 mol.) and a little zinc chloride, condense to ethylic isopropylenemalonate,  $\text{CMe}_2\cdot\text{CH}(\text{COOEt})_2$ . This is a colourless liquid, boiling at 175—178° under 120 mm. pressure; when hydrolysed with 40 per cent. aqueous potash, it yields the acid, which melts at 170—171°.

C. F. B.

**Ethylic Dicarboxyglutaconate.** By SIEGFRIED RUHEMANN and A. P. SEDGWICK (*Ber.*, 1895, **28**, 822—825).—Ethylic dicarboxyglutaconate reacts with methylamine in the same manner as with aniline (this vol., i, 20), the products being ethylic methylamidoethylenedicarboxylate,  $\text{NHMe}\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$ , melting at 34°, and the methylamide of malonic acid. Ethylenediamine behaves in a similar manner, ethylic ethylenediamidodiethylenetetracarboxylate,



which crystallises in prisms melting at 126°, being formed along with ethylenemalonamide. Ethylic metaphenylenediamidodiethylenetetracarboxylate,  $\text{C}_6\text{H}_4[\text{NH}\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2]_2$ , is obtained when metaphenylenediamine is employed. It crystallises in needles, and melts at 110°. Formamide, on the other hand, converts ethylic dicarboxyglutaconate into ethylic dihydroxypyridinedicarboxylate,



which crystallises in slender, colourless needles, and melts at 201°. This substance combines with bromine to form a yellow additive compound, which loses all its bromine in a vacuum.

A. H.

**Dibasic Ketonic Acid,  $\text{C}_{10}\text{H}_{14}\text{O}_6$ .** By E. HOFACKER and EDUARD A. KEHRER (*Ber.*, 1895, **28**, 917—921).—The preparation of  $\delta$ -furfurylidenelevulinic acid has been previously described (*Abstr.*, 1893, i, 254); it is separated from  $\beta\delta$ -difurfurylidenelevulinic acid by repeated treatment with hot water, in which the latter is less soluble. By the action of hydrogen chloride on the  $\delta$ -acid in alcoholic solution, ethylic para- $\phi$ -diketosebate,  $\text{C}_2\text{H}_4(\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOEt})_2$ , is formed; it

crystallises in colourless, lustrous, rhombic plates, and melts at  $46^{\circ}$ . The *methylic salt* resembles the preceding compound, and melts at  $92^{\circ}$ . The *acid* is most readily prepared by hydrolysis of the ethereal salts with concentrated hydrochloric acid; it crystallises from water in colourless plates, melts at  $156\text{--}157^{\circ}$ , reduces Fehling's solution when heated, becomes yellow with sulphuric acid, and yields iodoform. The *silver salt* is amorphous; the *zinc salt* forms silvery plates. By the action of alcoholic potash on the above ethereal salts, the preceding compound is formed, together with a second acid, which dissolves more readily in ether, and is obtained as a bye-product during the preparation of the ethereal salts. It melts at  $89\text{--}90^{\circ}$ , yields crystalline *calcium* and *zinc salts*, and is being further investigated.

J. B. T.

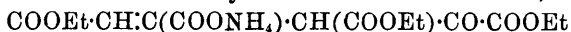
### Formation of Propyltartronic acid from Dibutyl dicyanides.

By KARL BRUNNER (*Monatsh.*, 1894, **15**, 747—774; compare *Abstr.*, 1893, **i**, 553).—*Propyltartronic acid*,  $\text{CH}_2\text{Et}\cdot\text{C}(\text{OH})(\text{COOH})_2$ , prepared from the dibutyl cyanide obtained from normal butyric anhydride, crystallises in monoclinic plates containing  $1\text{H}_2\text{O}$ , melts at  $52\text{--}56^{\circ}$ , and decomposes with evolution of gas at  $105^{\circ}$ . The anhydrous acid melts at  $122^{\circ}$ , is soluble in water and alcohol, and on distillation yields carbonic anhydride and  $\alpha$ -hydroxyvaleric anhydride.

*Isopropyltartronic acid*,  $\text{CHMe}_2\cdot\text{C}(\text{OH})(\text{COOH})_2$ , obtained from isobutyric anhydride, melts and decomposes at  $149^{\circ}$ , and is converted at  $150^{\circ}$  into carbonic anhydride and  $\alpha$ -hydroxyisovaleric acid, which melts at  $83^{\circ}$  (compare this vol., **i**, 21).

G. T. M.

**Action of Ammonia on Ethylic Oxalacetate.** By WILHELM WISLICENUS and WALTER BECKH (*Ber.*, 1895, **28**, 788—791).—Ammonia combines with ethylic oxalacetate in cold alcoholic or ethereal solution forming a compound  $\text{COOEt}\cdot\text{C}(\text{ONH}_2)\cdot\text{CH}\cdot\text{COOEt}$  or  $\text{COOEt}\cdot\text{C}(\text{OH})(\text{NH}_2)\cdot\text{CH}_2\cdot\text{COOEt}$ . This is a white, crystalline powder, which melts at  $83^{\circ}$ , and exhibits many of the reactions of an ammonium salt; it readily decomposes when kept or when heated, yielding the ammoniumtriethylic salt of aconitoxalic acid,



(Claisen and Hori, *Abstr.*, 1891, 424). This *ammonium salt* melts at  $129^{\circ}$ , the *barium salt* at  $213\text{--}215^{\circ}$ ; the *calcium salt* crystallises with  $2\text{H}_2\text{O}$ .

C. F. B.

**Butanetetracarboxylic Acids.** By KARL AUWERS and TITUS V. BREDT (*Ber.*, 1895, **28**, 882—890; compare *Abstr.*, 1894, **i**, 362).—Butanetetracarboxylic acids are formed only in small quantity by the action of iodine on ethylic sodioethenyltricarboxylate; the hexacarboxylate, which is first obtained, is hydrolysed and carbonic anhydride eliminated. The acids were therefore prepared in the manner previously described (*h* and *n* signifying the acid of higher and of lower melting point).

The *n*-tetramide,  $\text{C}_4\text{H}_8(\text{CONH}_2)_4$ , is readily obtained by the interaction of the *n*-tetramethylic salt and ammonia, or by heating the

acid with alcoholic ammonia at 135—145°; at higher temperatures resinous products are formed, at lower temperatures unaltered ammonium salt separates. The compound is very sparingly soluble, crystallises in rhombic plates, turns brown at 280°, and chars without melting at about 310°; it is hydrolysed by prolonged boiling with potash.

The *n*-diamic acid,  $C_4H_6(COOH)_2(CONH_2)_2$ , prepared by the action of ammonia on the diethylic salt, is purified by means of its crystalline sodium salt, and is deposited in thin plates melting and evolving gas at 181°; it is rapidly decomposed by water, and is insoluble in other media. The diimide,  $C_4H_6\left(\begin{smallmatrix} CO \\ CO \end{smallmatrix} > NH\right)_2$ , is prepared by heating the preceding compound above its melting point, and is formed together with the tetramide, from which it is separated by its solubility in nitrobenzene; it is sparingly soluble, crystallises from water in small, hexagonal plates, and chars at about 320° without melting. The imide is soluble in soda and ammonia; its silver salt is white and sparingly soluble; when reduced, it is converted into an oily base which has a characteristic odour and yields a crystalline platinumchloride.

The diamilic acid,  $C_4H_6(COOH)_2 \cdot (CO \cdot NHPh)_2$ , is prepared from the anhydride (m. p. 247°) and aniline; it crystallises in broad, truncated needles, melts, when rapidly heated, at 187°, and evolves gas at 190°.

The diphenylimide,  $C_4H_6\left(\begin{smallmatrix} CO \\ CO \end{smallmatrix} > NPh\right)_2$ , is formed by heating the preceding compound at about 190°, and is deposited from dilute acetic acid in rhombic crystals melting at 194—197°. The tetraphenylhydrazide,  $C_4H_6(CO \cdot NH \cdot NHPh)_4$ , prepared from the tetrathylic salt and phenylhydrazine, is sparingly soluble, forms small, colourless prisms, and melts above 280°.

All attempts to prepare the *h*-tetramide were unsuccessful. Diethylic *h*-butanetetra-carboxylate,  $C_4H_6(COOH)_2 \cdot (COOEt)_2$ , is formed by the action of hydrogen chloride on the *h*-acid in alcoholic solution at 0°; it is a colourless oil, and when treated with ammonia yields the *h*-diamide, which closely resembles the isomeric compound, is even more readily hydrolysed, and melts at 169°. When heated above its melting point, or by the action of alcoholic ammonia on the *h*-acid at 135—145°, the diimide is formed (see above), proving the previous conversion of the *h*- into the *n*-acid. The *h*-diamilic acid, prepared from aniline and the anhydride (m. p. 168°), crystallises in long, slender needles, and melts at 167°. When heated above its melting point, a compound is formed, which appears to be a mixture of *h*- and *n*-diphenylimides, it crystallises in plates, softens at 180°, and melts between 210° and 230°. The *h*-tetraphenylhydrazide crystallises in small, slender, colourless needles, and melts above 280°.

Both the butanetetra-carboxylic acids combine with resorcinol or dimethylmetamidophenol; the resulting dyes resemble those from succinic acid.

J. B. T.

**Dimethylvioluric acid and Dimethylnitrobarbituric acid.**  
By RUDOLF ANDREASCH (*Mcnatsh.*, 1895, 16, 17—33; compare Abstr.,

1879, 618, and Techow, this vol., i, 83).—Dimethylvioluric acid (dimethylisonitrosomalonylcarbamide),  $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} > \text{C} : \text{N} \cdot \text{OH}$ , prepared from dimethylalloxan and hydroxylamine hydrochloride at  $100^\circ$ , crystallises from water in needles which contain  $1\text{H}_2\text{O}$  and melt at  $141^\circ$ . It forms a neutral *potassium* salt,  $\text{C}_6\text{H}_5\text{KN}_3\text{O}_4$ ,  $\text{C}_6\text{H}_7\text{N}_3\text{O}_4$ , which forms slender, orange-red needles; a *sodium* salt, with  $4\text{H}_2\text{O}$ , which crystallises in peach-blossom-red needles; an *acid sodium* salt,  $\text{C}_6\text{H}_5\text{NaN}_3\text{O}_4$ ,  $\text{C}_6\text{H}_7\text{N}_3\text{O}_4$ , which crystallises in orange-red needles; an *ammonium* salt, in red needles; a *barium* salt, with  $4\text{H}_2\text{O}$ , which crystallises in garnet-red scales; and a *strontium* salt, with  $2\text{H}_2\text{O}$ , which crystallises in red needles. The *zinc*, *lead*, *cadmium*, and *silver* salts are all coloured and crystallise well, and the *ferrous* salt yields a dark blue aqueous solution.

*Dimethylnitrobarbituric acid*,  $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} > \text{CH} \cdot \text{NO}_2$ , is obtained on mixing together dimethylvioluric acid and nitric acid. It dissolves in 5.98 parts of water at  $14^\circ$ , and separates from the solution in needles or in crystalline masses, melts with decomposition at  $131$ – $132^\circ$ , and yields the following salts:—A *potassium* salt,  $\text{C}_6\text{H}_5\text{N}_3\text{O}_5\text{K}$ , which crystallises in greenish-yellow needles; a *sodium* salt, with  $1\text{H}_2\text{O}$ , in yellow needles; an *ammonium* salt, crystallising in slender needles; a *calcium* salt, in flat prisms; a *barium* salt, with  $2\text{H}_2\text{O}$ , in rosy-red, flat needles; a *strontium* salt, crystallising in light cornflower-blue masses; a *magnesium* salt, with  $4\text{H}_2\text{O}$ , which crystallises in yellowish-green needles; a *lead* salt, in bright yellow scales; and a *silver* salt, which forms violet-grey prisms.

G. T. M.

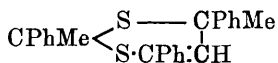
**Synthesis of Sulphones from Sodium Alkyl Sulphates by the Action of Potassium Alkyl Sulphates.** By ROBERT OTTO (*Annalen*, 1895, 284, 300–306).—In the well-known synthesis of sulphones by acting on sodium alkyl sulphates with alkyl haloids, it is found that the latter may be replaced by potassium alkyl sulphates. The method, however, is only of theoretical interest, and has no practical advantages over the older process.

M. O. F.

**Thiophen Derivatives.** By EUGEN BAUMANN and EMIL FROMM (*Ber.*, 1895, 28, 890–895).—Paradimethoxystilbene is readily converted into paratetramethoxytetraphenylthiophen by heating with sulphur; other compounds with the group  $\text{CH}:\text{CH}$  readily react, but saturated compounds are unaltered, or practically so, even at very high temperatures.

Cinnamic acid and sulphur, when heated at  $240^\circ$ , evolve hydrogen sulphide and carbonic anhydride; the product, after purification, melts at  $126$ – $128^\circ$ , and consists of 2:5- and 2:4-diphenylthiophens, which can be separated by crystallisation from alcohol and acetone; the former melts at  $152^\circ$  and is already known; the latter melts at  $119$ – $120^\circ$ , crystallises in colourless, lustrous plates, and differs but little

in solubility from the isomeric compound; its constitution is shown by its formation from anhydrotriacetophenone bisulphide,



(compare this vol., i, 362). Sulphur dissolves in boiling cinnamene, and at 190—195° evolution of hydrogen sulphide commences, above 200° ethylbenzene is formed, and the residue consists of 2:4-diphenylthiophen together with the 2:5-isomeride in very small quantity.

J. B. T.

**Formation of Carbon Rings: Conversion of Pimelic into Cyclopentenedicarboxylic acid.** By RICHARD WILLSTÄTTER (*Ber.*, 1895, **28**, 655—665; compare Haworth and Perkin, *Trans.*, 1894, 978).— $\alpha,\alpha$ -Dibromopimelic acid,  $\text{COOH} \cdot \text{CHBr} \cdot [\text{CH}_2]_3 \cdot \text{CHBr} \cdot \text{COOH}$ , is obtained by heating pimelic acid with bromine and phosphorus; it melts at 140—142°, and is very soluble in alcohol and ether, dissolving with difficulty in cold water but more readily in hot. It resists the action of hot aqueous soda, and does not yield silver bromide when boiled with fuming nitric acid in presence of silver nitrate. The diethyl salt is a heavy, colourless oil which boils at 224° (corr.) under a pressure of 28 mm.

$\Delta^1$ -1:2-Cyclopentenedicarboxylic acid, obtained by the action of sodium ethoxide on diethyl dibromopimelate, is identical with dihydropentenedicarboxylic acid (*loc. cit.*). The anhydride is a colourless oil which yields the acid on treatment with boiling water. The normal silver salt,  $\text{C}_7\text{H}_6\text{O}_4\text{Ag}_2$ , is obtained as a white precipitate on adding silver nitrate to a neutral solution of the sodium salt.  $\alpha,\alpha$ -Dibromo-1:2-cyclopentenedicarboxylic acid (*loc. cit.*) is obtained by allowing the unsaturated acid to remain in an atmosphere of bromine vapour. When heated with concentrated aqueous potash, cyclopentenedicarboxylic acid is converted into adipic acid.

The ethylic salt of dibromosuberlic acid is a colourless oil which boils at 233—236° (corr.) under a pressure of 26 mm. When treated with sodium ethoxide, it yields diethoxysuberlic acid together with a small quantity of dihydroxysuberlic acid; tetrahydrophthalic acid is not present in the mixture.

M. O. F.

**Hexamethylene Derivatives.** By ALPHONSE COMBES (*Bull. Soc. Chim.*, 1894, [3], **11**, 710—717).—Triethyltriketohexamethylene (triethylphloroglucinol),  $\text{CO} < \begin{array}{c} \text{CHEt} \cdot \text{CO} \\ \text{CHEt} \cdot \text{CO} \end{array} > \text{CHEt}$ , is obtained by heating pure butyric and aluminium chlorides together at 60°, and is insoluble in water, but soluble in chloroform; it melts at 107°, and boils at 216° (15 mm.). If the reaction is carried out in chloroform solution, the yield is very small, the main products being butyric acid and butyrene, possibly from the decomposition of an intermediate product,  $\alpha$ -butyrylbutyric chloride.

Triethylphloroglucinol behaves as a monobasic acid, the mon-alkali salts being neutral; other more basic salts probably exist, as heat is developed on the addition of more alkali. It does not react with the



usual reagents for hydroxyl, and is stable towards potash at 100°, but it is completely hydrolysed by 25 per cent. aqueous potash at 150—160° into butyrene, butyric acid, and carbonic anhydride; phloroglucinol behaves in a precisely similar manner under the same conditions, yielding acetone and acetic acid. The *phenylhydrazone* crystallises with difficulty. When triethylphloroglucinol is distilled with zinc dust, it is reduced to various hydrocarbons, including a small quantity of triethylbenzene, in this also resembling phloroglucinol, which yields only a small quantity of benzene under the same conditions. The behaviour towards ferric chloride, too, is similar to that of phloroglucinol, there being no coloration except in concentrated solutions.

The formation of the ring may possibly result from condensation of an intermediate product,  $\text{COPr}^{\alpha}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{CHEt}\cdot\text{COCl}$ .

JN. W.

**Diketoexamethylene from Succinic acid.** By FRANZ FEIST (*Ber.*, 1895, **28**, 738—741).—Anhydrous calcium succinate was heated in a Meer's retort, and the distillate distilled with steam; the residue was repeatedly treated with hot water, and the ketone isolated from the solution by means of sodium hydrogen sulphite. The compound was identified by its action on Fehling's solution and potassium permanganate, by the preparation of the characteristic phenylhydrazone, and by the formation of quinone when treated with ferric chloride. The yield was only 0.4—0.5 gram from 1 kilo. of succinic acid.

J. B. T.

**Synthesis of Naphthenes.** By NICOLAI D. ZELINSKY (*Ber.*, 1895, **28**, 780—783).—By distilling dimethylpimelic acid (Abstr., 1892, 430) with lime, 1 : 3-dimethylketoexamethylene,  $\text{CH}_2<\text{CH}_2\cdot\text{CHMe}>\text{CO}$ , is obtained; it boils at 173—174°, yields an *oxime* melting at 104—105°, and can be reduced to a *secondary alcohol* boiling at 174.5° under 755 mm. pressure. This yields an *iodide*, by reduction of which 1 : 3-dimethylhexamethylene,  $\text{CH}_2<\text{CH}_2\cdot\text{CHMe}>\text{CH}_2$ , can be obtained.

1 : 3-Dimethylhexamethylene boils at 119.5° under 751 mm. pressure, and has a sp. gr. = 0.7688 at 19°/0°; it is probably identical with Markovnikoff's  $\alpha$ -octonaphthene from Caucasian naphtha. Its reactions are those of a saturated aliphatic hydrocarbon; with bromine and aluminium bromide, however, it yields tetrabromo-1 : 3-xylene, and with a mixture of nitric and sulphuric acids, it yields a trinitro-1 : 3-xylene.

C. F. B.

**The Benzene Nucleus.** By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **51**, 444—446; compare Abstr., 1894, i, 325, 501).—Among the diamido- and dihydroxy-benzenes the meta-derivative is the most soluble, the para-derivative being the least soluble; so, also, terephthalic acid is the least soluble of the three dicarboxylic acids, but the ortho-acid is more soluble than the meta-acid. A comparison

may be drawn between the solubility of the phthalic acids and that of the dicarboxylic acids of the fatty series. For, according to the author's configuration for benzene (Abstr., 1894, i, 326), fumaric acid has a similar structure to terephthalic acid, maleic acid to the meta-acid, and acetylenedicarboxylic acid to the ortho-acid; it may thus be expected that the order of solubility will be acetylenedicarboxylic acid, maleic acid, fumaric acid; and this is found to be the case.

The author can also explain the exceptional behaviour of ortho-toluidineparasulphonic acid towards acetic anhydride (Abstr., 1884, 1024), and the difference in the solubilities of the aniline and toluidine sulphonic acids, by reference to his formula for benzene.

A. G. B.

**Alteration of Phenol by the Action of Light and the Formation of Hydrogen Peroxide.** By A. BACH (*Chem. Centr.*, 1894, ii, 318; from *Mon. Sci.*, [4], 8, 508—510).—It is well known that pure phenol by the action of light and air is gradually coloured red to brown, and this alteration has been attributed to the formation of hydrogen peroxide, which can usually be detected in the altered phenol. The author has found that when phenol is exposed to the action of light and moisture in an atmosphere of carbonic anhydride, it is quickly turned red, and no trace of hydrogen peroxide can be detected. On the other hand, when phenol is exposed to light and damp air, and care is taken to exclude carbonic anhydride, after three days only a faint, brownish coloration is observed, and hydrogen peroxide can then be detected by its characteristic reactions. Whence the author concludes that the alteration of the phenol is not due to the formation of hydrogen peroxide.

E. C. R.

**Aromatic Arsenites.** By P. FROMM (*Ber.*, 1895, 28, 620—623).—*Triphenylic arsenite* is prepared by adding arsenic trichloride dissolved in ether to sodium phenoxide suspended in the same medium. It is a colourless, viscous liquid of sp. gr. 1.354 at 20°; it boils at 275° under a pressure of 57 mm., and has the odour of phenol. The salt is decomposed by water into phenol and arsenious anhydride, whilst the action of chlorine and bromine gives rise to substituted derivatives of phenol.

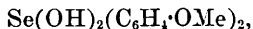
*Triparatolylic arsenite* is prepared by a similar method, xylene being employed instead of ether. It is a colourless, oily liquid of sp. gr. 1.2794 at 13°; it boils at 290° under a pressure of 20 mm., and is readily decomposed by water.

*Tri-β-naphthyllic arsenite* crystallises in long, colourless needles, and melts at 113—114°; boiling water decomposes it into β-naphthol and arsenious anhydride.

*Tribenzylic arsenite* is a yellow, viscous liquid which partly decomposes when distilled at 200° under a pressure of 20 mm. Benzylic alcohol and arsenious anhydride are formed when the salt is treated with water, and the action of bromine gives rise to bromobenzoic acid, benzylic bromide, arsenious anhydride, and arsenic tribromide.

M. O. F.

**Some Selenium Derivatives of Anisoil and Phenetoil.** By FRANZ KUNCKELL (*Ber.*, 1895, **28**, 609—612).—When selenyl chloride,  $\text{SeO}_2\text{Cl}_2$  (1 mol.), is added slowly to an ethereal solution of anisoil (2 mols.), *dichloroselenoanisoil*,  $\text{SeCl}_2(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , and *selenoanisoil*,  $\text{Se}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , are obtained. The former crystallises in yellow needles, and melts at  $159^\circ$ ; the latter in white nacreous plates, melting at  $48^\circ$ . The latter, in chloroform solution, unites with chlorine to form the first-mentioned compound; with bromine to form *dibromoselenoanisoil*, brick-red needles, melting at  $124^\circ$ , whilst with iodine it yields a red syrup. By treating the halogen compounds with moist silver oxide, they can be converted into *dihydroxyselenoanisoil*,



which crystallises in white needles, and melts at  $137^\circ$ .

An analogous series of compounds can be prepared from phenetoil,  $\text{C}_6\text{H}_5\cdot\text{OEt}$ . *Selenophenetoil*, white needles, m. p.  $56^\circ$ . *Dichloroselenophenetoil*, yellow needles, m. p.  $140^\circ$ . *Dibromoselenophenetoil*, red needles, m. p.  $123^\circ$ . *Diiodoselenophenetoil*, coffee-coloured needles, m. p.  $96^\circ$ . *Dihydroxyselenophenetoil*, white needles, m. p.  $145^\circ$ .

C. F. B.

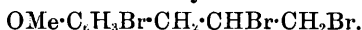
**Anethoïl.** By CARL HELL (*J. pr. Chem.*, 1895, [2], **51**, 422—424).—Some prefatory remarks to the following paper (see next abstract). The question whether anethoïl contains propenyl,  $\cdot\text{CH}:\text{CHMe}$ , or allyl,  $\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , receives additional importance from Eijkman's researches on the conversion of allylbenzene into propenylbenzene derivatives (*Abstr.*, 1890, 748), and from Grimaux's observation that essence of tarragon does not contain anethoïl, but an isomeride, estragoïl, and that anethoïl is probably a stereoisomeride of Eijkman's methylchavicol (*Abstr.*, 1894, i, 120).

A. G. B.

**Action of Bromine on Anethoïl.** By CARL HELL and G. GÄRTNER (*J. pr. Chem.*, 1895, [2], 424—434; compare preceding abstract).—*Bromanethoïl dibromide*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}_3\text{H}_5\cdot\text{Br}_2$ , is obtained by dropping bromine into a well-cooled ethereal solution of anethoïl, evaporating, washing with alcohol, and crystallising from light petroleum. It forms thick, strongly refractive needles, melts at  $107$ — $108^\circ$ , and dissolves easily in benzene, chloroform, and carbon bisulphide. Zinc dust removes 2 atoms of bromine from the compound, producing a white powder which is probably a polymeride of bromanethoïl, for the same substance is formed when anethoïl is polymerised with strong sulphuric acid and treated with bromine in ethereal solution. The oxidation of bromanethoïl dibromide by chromic acid in glacial acetic acid leads to the formation of a *dibromoketone*, to which the formula  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{CHBrMe}$  or  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CHBr}\cdot\text{COMe}$ , must be assigned if bromanethoïl dibromide be a propenyl derivative of the form



but which must have the constitution  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , if bromanethoïl dibromide be an allyl derivative of the form



Its constitution remains unsettled, but the weight of evidence is in favour of the second of those given; the compound crystallises from light petroleum in yellowish laminae, and from alcohol in slender, white needles; melts at  $98^{\circ}$ , and is very soluble in glacial acetic acid, benzene, chloroform, and carbon bisulphide. By treatment with zinc dust in alcohol, the dibromoketone loses the bromine from the side-chain, and yields the corresponding *bromoketone*,



which crystallises in colourless needles, melts at  $99^{\circ}$ , and is freely soluble in ether, benzene, glacial acetic acid, and chloroform.

When the dibromoketone is heated with potassium acetate in alcoholic solution, it yields an *acetyl* derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{C}_3\text{H}_7\text{O}_2\text{Ac}$ . When similarly treated with ammonia, it yields orange-yellow crystals and yellowish-white crystals; the latter can be separated from the former by their insolubility in cold glacial acetic acid, and, when recrystallised from the hot acid, melt at  $210\text{--}211^{\circ}$ .

When the dibromoketone is oxidised with potassium permanganate, bromanistic acid  $[\text{COOH} : \text{Br} : \text{OMe} = 1 : 3 : 4]$  is obtained, a result which settles the orientation of the nucleal bromine atom. A ketonic acid was also obtained by the oxidation of the ketone derived from the anethoil with which the authors worked, but the ketone from a sample of anethoil which had been specially prepared from star-anise oil did not yield such an acid. A. G. B.

### Action of Sulphuryl Chloride on Phenols and their Ethers.

By ALBERTO PERATONER and A. GENCO (*Gazzetta*, 1894, **24**, ii, 375—396).—Peratoner and Finocchiaro (Abstr., 1894, i, 368) have shown that in the chlorination of phenol, resorcinol, and phloroglucinol by sulphuryl chloride, the chlorine enters the molecule in the para-position relatively to the hydroxyl groups. Quinol should therefore not react with sulphuryl chloride; this is found to be the case if no solvent is employed, but on treating with sulphuryl chloride in ethereal solution, *orthodichloroquinol*,  $\text{C}_6\text{H}_2\text{Cl}_2(\text{OH})_2$ , is formed. It crystallises from water in long, reddish needles containing  $2\text{H}_2\text{O}$ , which are lost at  $100^{\circ}$ ; it melts at  $144^{\circ}$ , and sublimes unchanged. Its *dibenzoyl* derivative,  $\text{C}_6\text{H}_2\text{Cl}_2(\text{OBr})_2$ , crystallises in colourless scales melting at  $173\text{--}174^{\circ}$ .

*Orthodichloroquinone*,  $\text{C}_6\text{H}_2\text{Cl}_2\text{O}_2$ , may be prepared by oxidising the corresponding hydroxyl derivative by Clark's method; it crystallises in yellow laminae or needles melting at  $96^{\circ}$ , and is volatile in a current of steam.

On chlorinating quinol with smaller quantities of sulphuryl chloride than that used above, quinhydrone, monochloroquinol, quinone, its di- and tetra-chlorides, and chloranil are formed.

*Monochloroquinol dichloride*,  $\text{C}_6\text{H}_3\text{Cl}_3\text{O}_2$ , is obtained by the action of sulphuryl chloride on an ethereal solution of the monochloroquinol melting at  $104\text{--}105^{\circ}$ ; it forms colourless laminae which do not melt but sublime at  $195\text{--}200^{\circ}$ . When heated with acetic acid or dilute alcohol, it yields a mixture of the meta- and para-dichloroquinols; it

therefore has the constitution  $\begin{array}{c} \text{CH} \cdot \text{CO} \cdot \text{CHCl} \\ | \qquad | \\ \text{CCl} \cdot \text{CO} \cdot \text{CHCl} \end{array}$ ; no tetrachloride could be prepared, chloranil resulting from the further action of sulphuryl chloride.

Quinone dichloride is converted into a mixture of orthodichloroquinol and monochloroquinol by sulphurous acid. Monochloroquinol and quinone tetrachloride under similar conditions yield trichloroquinol.

W. J. P.

### Formation of Tetrachloroquinone from Hexachlorophenol.

By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1894, [3], **11**, 705—710).— $\alpha$ -Hexachlorophenol is hydrolysed by water or acids into tetrachloroquinone and pentachlorophenol, but is converted by chromic acid into the latter substance alone. When heated with water for 24 hours at 160—165°, carbonic anhydride is liberated, and after the pentachlorophenol and unchanged hexachlorophenol have been dissolved out with light petroleum, the residual tetrachloroquinone merely requires to be washed with water. The yield is not large, but the product is very pure. A quantitative yield is obtained by heating the well-powdered substance with five or six times its weight of concentrated sulphuric acid, diluted with 1 or 2 per cent. of water. The product is washed with water, and dried at the ordinary temperature, no organic bye-products being formed.

J. W.

**Action of Alkalis on Brominated Derivatives of Phloroglucinol.** By JOSEF HERZIG and J. POLLAK (*Monatsh.*, 1894, **15**, 700—704).—In contrast to the behaviour of tribromophloroglucinol, the true bromo-compounds of phloroglucinol derivatives, such as tribromodiethylphloroglucinol (m. p. 62—64°) and tribromotriethylphloroglucinol (m. p. 102—104°), are perfectly stable in presence of boiling solutions of caustic alkalis. Tribromotriethylphloroglucinol, when heated in sealed tubes with alcoholic potash at 140°, loses no bromine, but is converted into tribromodiethylphloroglucinol. A considerable quantity of phloroglucide,  $\text{C}_{12}\text{H}_{10}\text{O}_5 + 2\text{H}_2\text{O}$ , is formed as a bye-product in the preparation of diethylphloroglucinol (compare Will and Albrecht, *Ber.*, **17**, 2098).

G. T. M.

**Paramidobenzyllic Alcohol.** By OTTO FISCHER and GUSTAV FISCHER (*Ber.*, 1895, **28**, 879—881; compare *Abstr.*, 1891, 695).—The substance obtained after reducing paranitrobenzyllic acetate with stannous chloride, and removal of the tin by hydrogen sulphide, is shown to be diparamidobenzyllic sulphide,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{S}$ , and not paramidobenzyllic alcohol. The pure substance melts at 104—105°, and not at 95° as previously stated. Its formation is due to the action of the hydrogen sulphide on the amido-alcohol which is first formed. It forms a hydrochloride,  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{S} \cdot 2\text{HCl}$ , and a hydrobromide,



Paramidobenzyllic alcohol may be obtained by reducing a neutral solution of the nitro-alcohol with zinc dust. It forms large, colourless plates, melts at 65°, and readily reacts with aldehydes forming

condensation products. The *benzylidene* compound crystallises in yellowish plates melting at 67—68°.

*o*-Hydroxybenzylideneamidobenzyl alcohol, from salicylaldehyde and the amido-alcohol, forms golden plates and melts at 155°.

*Benzoylamidobenzyl alcohol* forms colourless crystals and melts at 150—151°.

The amido-alcohol may readily be converted into diparamidobenzyl sulphide by saturating an acidified solution of the alcohol with hydrogen sulphide.

J. J. S.

**Reduction of Nitrobenzyl Chloride.** By OTTO DIMROTH and JOHANNES THIELE (*Ber.*, 1895, **28**, 914—916).—When ortho- and para-nitrobenzyl chlorides are reduced with stannous chloride at low temperatures, and the product treated with hydrogen sulphide, they yield the corresponding diamidobenzyl sulphides; the ortho-compound has been described by Jahoda and also by Gabriel (this vol., i, 190); the para-derivative is identical with the “paramidobenzyl alcohol” prepared by O. and G. Fischer (*Abstr.*, 1891, 695, and preceding abstract). Both compounds readily lose hydrogen sulphide when treated with salts of the heavy metals. The nature of the action by which the sulphides are formed is not understood; probably the intermediate compounds  $C_6H_4 \begin{smallmatrix} CH_2 \\ | \\ NH \end{smallmatrix}$  [ $CH_2:NH = 1:4$  and  $1:2$ ] are

first produced; it is improbable that the chlorides, acetates, or alcohols directly condense with hydrogen sulphide, and direct experiments with orthamidobenzyl alcohol and orthamidobenzyl chloride confirm this.

J. B. T.

**Cyaphenine; Substituted Benzonitriles.** By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], **51**, 399—414).—Trinitrocyaphenine crystallises in small needles, and is nearly insoluble in all ordinary solvents. It melts and decomposes between 250° and 260°; unlike cyaphenine, it is very easily hydrolysed, metanitrobenzoic acid being produced.

Attempts to polymerise the nitrobenzonitriles by treating them with fuming sulphuric acid failed, a more deeply-seated reaction occurring in each case, and a study of the polymerisation of benzonitrile itself by this method showed that the highest yield was 10 per cent. of cyaphenine.

Metanitrobenzonitrile yields metanitrobenzamide when warmed with sulphuric acid; the amide melts at 143° and boils at 310—315°; its crystallographical measurements are given. When the nitrile is treated with fuming sulphuric acid, it yields *dimetanitrobenzoylimide*,  $(NO_2 \cdot C_6H_4 \cdot CO)_2NH$ , which crystallises in colourless tablets, and usually melts at 199°, but at 120° when it is kept at this temperature for a long time, and at 80° when allowed to solidify again; it is very sparingly soluble except in glacial acetic acid and in acetone; its crystallographical measurements are given.

With ordinary sulphuric acid, paranitrobenzonitrile behaves similarly to the meta-derivative, but with the fuming acid it suffers a more deeply-seated change, the nature of which was not determined.

Orthonitrobenzonitrile is more easily attacked by sulphuric acid than are its isomerides, and the change which occurs is of a complex character. By using an acid of sp. gr. 1.6 the nitrile can be converted into orthonitrobenzamide, which melts at  $174^{\circ}$  and distils unchanged at  $317^{\circ}$ .

Sodium is practically without action on metanitrobenzonitrile in ether; similarly, this nitrile is remarkably stable towards nitrating agents and bromine. Attempts to polymerise the halogen-benzonitriles have also failed.

It is already known that the presence of a nitro-group in the ortho or para-position relatively to the amido-group of a substituted aniline renders diazotisation of the compound difficult, and that pentabromaniline is not susceptible of diazotisation; since, on the other hand, the symmetrical trihalogen-anilines do not show this difficulty, it is surprising to find that 2 : 3 : 5 : 6-tetrabromaniline behaves like pentabromaniline towards diazotising agents. This tetrabromaniline was prepared by reducing *tetrabromonitrobenzene*,  $[\text{NO}_2 : \text{Br}_4 = 1 : 2 : 3 : 5 : 6]$ , which crystallises in small, colourless laminae, and melts at  $168^{\circ}$ ; the aniline forms colourless needles, melts at  $130^{\circ}$ , and yields bromanil by oxidation.

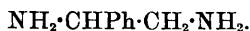
The author concludes with some remarks on the mechanism of the hydrolysis of nitriles into acids, a reaction which, he believes, occurs in two stages—the formation of an amide and the hydrolysis of this (compare Sudborough, *Proc.*, 1895, 74).

A. G. B.

**Hydrolysis of Aromatic Nitriles.** By JOHN C. CAIN (*Ber.*, 1895, 28, 967—969).—Dinitrodurene,  $\text{C}_6\text{Me}_4(\text{NO}_2)_2$   $[\text{NO}_2 : \text{NO}_2 = 1 : 4]$ , is obtained by nitrating durene at  $15^{\circ}$  in presence of a large excess of fuming sulphuric acid. In addition to diamidodurene, which melts at  $149^{\circ}$ , reduction with zinc dust and glacial acetic acid gives rise to *amidonitrodurene*, which crystallises from alcohol in yellow needles and melts at  $158$ — $159^{\circ}$ . This is converted by means of the Sandmeyer reaction into the *nitrile* of nitrodurene-carboxylic acid, which crystallises from alcohol in white needles and melts at  $160^{\circ}$ . Attempts to hydrolyse the nitrile with hydrochloric acid have not hitherto been successful, although an acid substance melting at  $105^{\circ}$  has been obtained by the action of soda.

M. O. F.

**Reduction of Amidonitriles.** By ATTILIO PURGOTTI (*Gazzetta*, 1894, 24, ii, 427—431).—On reducing the amidonitrile prepared from the cyanhydrin of benzaldehyde with zinc dust and hydrochloric acid, a base is obtained; the analyses of the platinochloride and of the benzoyl derivative point to its being *phenylethylenediamine*,

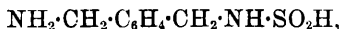


The investigation is being continued.

W. J. P.

**Action of Thionylaniline on the Xylylenediamines.** By FRZ. DÜRING (*Ber.*, 1895, 28, 600—608).—The xylylenediamines,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NH}_2)_2$ , react with thionylaniline,  $\text{SO} \cdot \text{NPh}$ , yielding

ammonia and aniline and a precipitate which consists of the thio-sulphate and trithionate of the diamine, which are soluble in water, and amidotolualdehyde,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH}_2$ , which is insoluble. In the 1 : 2-series this precipitate is entirely soluble in water, and contains no amidotolualdehyde, but dihydroisoindeole,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{NH}$ , instead, and diamine sulphate in place of thiosulphate. With sulphurous anhydride, the diamines, in ethereal solution, yield dithionamic acids,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NH} \cdot \text{SO}_2\text{H})_2$ ; but these, especially the 1 : 2-derivative, readily lose  $\text{SO}_2$ , forming the monothionamic acids,

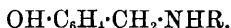


which yield crystalline compounds with benzaldehyde (1 mol.).

The *phenylhydrazones* of 1 : 3- and 1 : 4-amidotolualdehyde are yellow, and melt respectively at  $253^\circ$  and  $278^\circ$ . The other substances are white and, so far as their behaviour when heated is described, either do not melt or are decomposed.

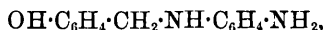
C. F. B.

**Action of Orthohydroxybenzylic Alcohol (Saligenin) on Aromatic Diamines.** By CARL PAAL and H. RECKLEBEN (*Ber.*, 1895, 28, 934—936; compare C. Paal and H. Senninger, *Abstr.*, 1894, i, 450).—Primary diamines behave as monamines towards this alcohol, condensing with it to products of the type



These are rather unstable, crystalline substances, which decompose soon after melting, and are both phenolic and basic in character. The solutions in mineral acids give a blue thionine reaction with hydrogen sulphide and ferric chloride.

*Orthohydroxybenzylorthophenylenediamine*,

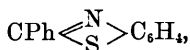


crystallises from alcohol in yellowish, concentrically grouped needles, and melts at  $157^\circ$ . It is sparingly soluble in water or light petroleum, easily in the other usual solvents, and in acids and alkalis; the acid solutions give a red coloration with ferric chloride. The *diacetyl* compound,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$ , from the base and the boiling acid or cold anhydride, crystallises from alcohol in white needles, and melts at  $162^\circ$ ; it is slowly hydrolysed by acids and alkalis. The *triacetyl* derivative, obtained by acting on the base with boiling acetic anhydride, forms colourless, well-defined crystals, and melts at  $133^\circ$ ; it is insoluble in alkalis and dilute acids, but is slowly hydrolysed by boiling alkalis. *Orthohydroxybenzylorthotolylenediamine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$  [ $\text{NH} : \text{NH}_2 : \text{Me} = 1 : 2 : 4$  or  $1 : 2 : 5$ ], crystallises in small, felted needles, and melts at  $167^\circ$ . *Orthohydroxybenzylparaphenylenediamine* is very unstable in presence of water. It crystallises from alcohol in small, yellow, concentrically grouped needles, and melts at  $119^\circ$ .

JN. W.



**Benzenylamidothiophenol.** By ERNEST NÆGELI (*Bull. Soc. Chim.*, 1894, [3], 11, 893—897).—Benzenylamidothiophenol,



from benzanilide and sulphur, melts at  $113^\circ$  (uncorr.); (compare Hofmann, *Ber.*, 12, 2360, and 13, 1236). The *mononitro-derivative* melts at  $188^\circ$ , and on fusion with potash yields paranitrobenzoic acid; the nitro-group is therefore in the para-position relatively to the benzylic carbon. JN. W.

**Mixed Amidines and Tautomerism.** By HANS V. PECHMANN (*Ber.*, 1895, 28, 869—879; compare *Abstr.*, 1894, i, 452 and 457).—In previous papers, the author has shown that mixed phenyltolylformazyls,  $\text{C}_7\text{H}_7\cdot\text{N}:\text{N}:\text{CR}:\text{N}:\text{NHPh}$  and  $\text{Ph}\cdot\text{N}:\text{N}:\text{CR}:\text{NH}\cdot\text{C}_7\text{H}_7$ , are identical, so far as regards their physical and chemical properties. In the present paper, it is shown that mixed amidines and diazoamidocompounds also exist in only one form, even when prepared by different methods, but that they can give isomeric ethyl and benzoyl derivatives.

*Phenylparatolylbenzenylamidine*,  $\text{PhN}:\text{CPh}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , or



whether prepared from benzanilide and toluidine or from benzotoluidide and aniline, has the same properties, melts at  $132$ — $133^\circ$ , and forms a *benzoyl* derivative which melts at  $142^\circ$  and is sparingly soluble in ether and alcohol.

*Ethylparatolylamidophenylbenzenylimidine*,  $\text{PhN}:\text{CPh}\cdot\text{NEt}\cdot\text{C}_7\text{H}_7$ , was prepared by acting on benzaniline with phosphoric chloride, and then treating the product with ethylparatoluidine. The base forms large, flat, six-sided prisms, and melts at  $102^\circ$ . The iodide melts at  $226^\circ$ .

*Ethylphenylamidoparatolylbenzenylimidine*,  $\text{C}_7\text{H}_7\cdot\text{N}:\text{CPh}\cdot\text{NEtPh}$ , obtained from benzotoluidide, phosphoric chloride, and ethylaniline, melts at  $117^\circ$ , and forms an iodide which melts at  $226^\circ$ . A mixture of equal parts of the two ethyl bases melts at  $86^\circ$ .

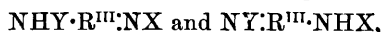
When the phenylparatolylbenzenylamidine, prepared by the two methods already given, was treated with ethylic iodide, a base was obtained in both cases, which melted at  $86^\circ$ , and was shown to be a mixture of the two ethylimidines (m. p.  $102^\circ$  and  $117^\circ$ ).

*Phenylparatolylethenylamidine*, prepared from thioacetanilide and paratoluidine hydrochloride and also from parathioacetotoluidide and aniline hydrochloride, crystallises in plates which melt at  $82$ — $83^\circ$ . It yields a *picrate*, melting at  $146$ — $147^\circ$ , and a *benzoyl* derivative, melting at  $96$ — $97^\circ$ . The latter is probably a mixture of the two possible isomerides, as, when decomposed by boiling with hydrochloric acid, it yields both benzanilide and benzotoluidide.

Diazoamidobenzenetoluene, prepared from diazobenzene and toluidine and also from diazotoluene and aniline, yields only a single acetyl derivative, *diazobenzeneparaacetotoluidide*,  $\text{PhN}:\text{N}\cdot\text{N}\cdot\text{Ac}\cdot\text{C}_7\text{H}_7$ . This base melts at  $140^\circ$ , and, when decomposed by acids, yields aceto-

toluidide, but no trace of acetanilide. The corresponding *benzoyl derivative*,  $\text{PhN:N} \cdot \text{NBz} \cdot \text{C}_7\text{H}_7$ , melts at  $124\text{--}125^\circ$ , and, when treated with acids, yields benzotoluidide, but not benzanilide.

The author argues that substances of the general type



where  $\text{R}^{\text{III}} = \text{N}$  (diaoamido compounds),  $\text{CH}$  (amidines) or  $\text{N} \cdot \text{CH} \cdot \text{N}$  (formazyl compounds), really exist in one form only, and that therefore the above formulæ cannot represent the structure of the molecule.

J. J. S.

**Stereoisomeric Diazocyanides.** By ARTHUR HANTZSCH and OTTO W. SCHULZE (*Ber.*, 1895, **28**, 666—676).—The cyano-derivatives of the diazo-series hitherto known are additive compounds of the general formula  $\text{R} \cdot \text{N}_2 \cdot \text{CN} \cdot \text{HCN}$ , which are prepared by adding a diazotised solution of the base to an excess of a well-cooled solution of potassium cyanide. Diazobenzene cyanide hydrocyanide,  $\text{PhN}_2 \cdot \text{CN} \cdot \text{HCN}$ , has already been described by Gabriel; it crystallises in pale yellow needles, and melts at  $70^\circ$ .

*Parachlorodiazobenzene cyanide hydrocyanide*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N}_2 \cdot \text{CN} \cdot \text{HCN}$ , forms light brown needles melting at  $103^\circ$ , whilst the corresponding *paranitrodiazobenzene cyanide hydrocyanide* crystallises in orange-coloured needles and melts at  $126^\circ$ . These compounds do not react with R-salt to form colouring matters.

When a slight excess of potassium cyanide solution is added to a well-cooled diazo-solution, true diazocyanides are formed. These exist in two modifications, the relations between which have led the author to consider them as being stereoisomeric, in the same way as the syn- and anti-diazosulphonates.

*Syn-chlorodiazobenzene cyanide*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \cdot \text{CN} \cdot \text{N}$ , is obtained, when the re-

action is carried out at a temperature below  $-5^\circ$ , in slender, yellow needles melting at  $29^\circ$ . It can be purified by dissolving it in alcohol below  $0^\circ$  and precipitating with ice-cold water. At the ordinary temperature, its alcoholic solution deposits the stereoisomeride of higher

melting point. *Anti-chlorodiazobenzene cyanide*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \cdot \text{N} \cdot \text{CN}$ , forms

yellow needles or brown prisms melting at  $105\text{--}106^\circ$ , and is obtained by the reaction between potassium cyanide and the diazo-salt when the solution is not well cooled. The anti-cyanide is also produced when the syn-compound is preserved in the dry state. Both the compounds are volatile with steam and insoluble in water. The behaviour of the two isomerides with finely divided copper, prepared by Gattermann's method, is characteristically different. When the syn-form is added to the powder mixed with water and a little alcohol, a very violent evolution of nitrogen, accompanied by small explosions, occurs, *para-chlorobenzonitrile*, which melts at  $92^\circ$ , being produced. The anti-cyanide, on the other hand, undergoes no change, and, when the mixture is heated, simply volatilises with the steam. The syn-derivative also appears to form metallic double cyanides much more

readily than the anti-form. The syn-cyanide readily gives an azo-colouring matter with  $\beta$ -naphthol in alcoholic solution, even in the absence of alkali, the product being identical with that obtained from the corresponding chloride. It also reacts in the usual way with R-salt, whilst the anti-cyanide does not yield colouring matters by either of these reactions. The syn-cyanide is converted by the action of aqueous alkalis into an additive product, which will be described in a subsequent communication.

*Syn-nitrodiazobenzene cyanide* is obtained at temperatures below  $-5^{\circ}$ , and forms a yellowish-brown, microcrystalline precipitate, melting at  $28-29^{\circ}$ . It is still less stable than the corresponding chlorinated derivative, and rapidly passes into the anti-modification.

*Anti-nitrodiazobenzene cyanide* forms red needles, melting at  $86^{\circ}$ , and is remarkably stable. These two substances closely resemble the chloro-derivatives described above. With copper powder, the syn-compound at once yields paranitrobenzonitrile, whilst the anti-form is not altered. The syn-modification readily forms colouring matters, whilst the anti-form reacts with  $\beta$ -naphthol and R-salt in a characteristically different manner. The syn-derivatives both explode when heated, whilst the anti-compounds do not.

The author rejects the formula  $N:NR:CN$  for one of the isomerides on account of the lack of probability that such a substance would so readily undergo molecular change, and because the substance in question differs so markedly from the substituted ammonium cyanides, which possess the same grouping, but are readily soluble in water and decomposed by carbonic anhydride, whilst the diazo-cyanides are insoluble in water and are not decomposed by carbonic anhydride.

A. H.

**Constitution of the Normal Diazo-compounds and of the Diazohalogen Salts.** By ARTHUR HANTZSCH (*Ber.*, 1895, 28, 676—687).—The author discusses the recently proposed formula  $R \cdot N \begin{smallmatrix} \diagup N \\ \diagdown Cl \end{smallmatrix}$

for the unstable series of compounds which are isomeric with the true diazo-compounds. The nature of the tetrazolium compounds and of the substituted ammonium compounds, both of which contain a pentad nitrogen atom, is urged against this interpretation of the relations between the two isomeric series. The complicated nature of the change from the unstable to the stable form, which actually goes on with extreme readiness and without the intervention of other substances, points in the same direction, as does also the formation of ring compounds of the type  $C_6H_4 \begin{smallmatrix} N \\ \diagdown O \end{smallmatrix} \diagup N$  from normal diazo-hydroxides without the sacrifice of their typical reactions.

The author considers that the halogen salts of the diazo-compounds must have a different constitution in the solid state from that which they have in aqueous solution.

The solid salts undergo gradual decomposition into nitrogen and the corresponding substituted hydrocarbon, when preserved at temperatures at which the solutions are quite unaltered. This is especially noticeable in the case of halogen-substituted diazo-salts.

*Diiododiazobenzene chloride* forms a lemon-yellow mass, which yields a neutral solution with water; this may be preserved for a considerable time, although the solid salt decomposes at the ordinary temperature, in the course of about 48 hours, into nitrogen and diiodochlorobenzene. *Trichlorodiazobenzene chloride* forms colourless prisms, and its aqueous solution is neutral. When the solid substance is exposed to sunlight, it decomposes into nitrogen and tetrachlorobenzene; this decomposition only proceeds very slowly in the dark. *Tribromodiazobenzene bromide* behaves in a precisely similar manner. With well-cooled aqueous potassium iodide, the diazobenzene salts give precipitates which probably consist of the corresponding iodides, although it has been found impossible to isolate them in the pure state. *Diiododiazobenzene iodide* is thus formed as a red, microcrystalline precipitate, which explodes in the dry state when touched. A solution of diiododiazobenzene chloride in water is quite stable, but, when potassium iodide is added, the diazo-iodide is precipitated, and at once decomposes quantitatively into nitrogen and triiodobenzene.

The aqueous solutions of these halogen-substituted diazo-salts, on the other hand, are remarkably stable. *Trichlorodiazobenzene chloride*, for example, may be boiled with water, or even with a mixture of hydrochloric and nitric acids, without undergoing any alteration, although the solution gives all the other typical diazo-reactions. This is to be explained, according to the author, by the supposition that the syn-diazo-salt, when dissolved in water, combines with a molecule of water and passes into the compound

$$\begin{array}{c} \text{Ph}\cdot\text{N} \\ \parallel \\ \text{HO}\cdot\text{N}\cdot\text{HCl} \end{array},$$

which may therefore be called the hydrochloride of syn-diazobenzene hydroxide.

On boiling with water, the hydrochloric acid is removed, and the typical syn-diazo-decomposition takes place, nitrogen being evolved and phenol formed. From this compound are also formed the various primary unstable syn-derivatives, which are all produced in the presence of alkaline substances, by which the hydrochloric acid is removed.

A. H.

**Diazo-compounds.** By EUGEN BAMBERGER (*Ber.*, 1895, 28, 826—837).—In the change of an isodiazocompound,  $\text{OH}\cdot\text{N}:\text{NR}$ , into one of the normal constitution,  $\text{N}:\text{NR}\cdot\text{OH}$ , in the presence of sulphuric acid, nitrous acid is liberated, and can be detected by blowing a current of air through the solution in which the change is going on, and then through an acid solution of potassium iodide and starch. It is therefore probable that the change consists in the decomposition of the isodiazohydroxide into a base and nitrous acid, which then react in the presence of acid to form the normal diazo-salt. Nitrous acid was detected in this way with paranitroisodiazobenzene, isodiazobenzene, orthonitroisodiazobenzene, and metanitroparaisodiazotoluene.

It appears that the isodiazohydroxide, which contains triad nitrogen, is produced when a free base (containing triad nitrogen) is acted on by nitrous acid; usually, this at once combines with a second mole-

cule of the base to form a diazoamido-compound. When the base is present as a salt, containing pentad nitrogen, the normal diazo-salt, which also contains pentad nitrogen, is produced.

The constitution of the diazo-ethers must be considered as still doubtful.

Griess appears to have had both isodiazo-compounds and bisdiazo-amido-compounds under his observation during his researches on the diazo-compounds. The substance described by Griess as parabromodiazobenzene potassium is, in reality, the iso-salt, and, when it is oxidised with potassium ferricyanide, yields parabromodiazobenzolic acid. The "diazobromobenzene," obtained by Griess from the potassium salt by the action of acetic acid, is the free isobromodiazobenzene hydroxide, and was considered by Griess to be identical with another substance which he obtained by the action of dilute aqueous potash on parabromodiazobenzene nitrate solution. The product of this last reaction is, in reality, bisparabromodiazobenzeneparabromanilide,  $C_6H_4Br \cdot N_2 \cdot NC_6H_4Br \cdot N_2 \cdot C_6H_4Br$ .

The power of preventing or greatly diminishing the formation of colouring matters from normal diazo-compounds, phenols, &c., which is possessed by strong acids, is shared by concentrated alkalis. In both cases the formation of colouring matter proceeds as usual after dilution.

The author also replies to the criticism of Hantzsch (this vol., i, 349), explaining that, in his view, the so-called "ring" diazo-compounds, of the type  $C_6H_4 \cdot \begin{smallmatrix} N:N \\ SO_2 \end{smallmatrix} > O$ , must now be considered to have the

"normal" structure,  $C_6H_4 \cdot \begin{smallmatrix} N:N \\ > O \\ SO_2 \end{smallmatrix}$ .

A. H.

**Isomerism in the Azo-series.** By EUGEN BAMBERGER (*Ber.*, 1895, 28, 837—854).—Numerous diazoamido-compounds have been prepared from the normal- and iso-diazo-derivatives, and in every case it has been found that the two products are identical. Paranitrodiazoamidobenzene has been previously described. *Paranitrodiazoamidotoluene* melts at 158·5—161·5° and crystallises from alcohol in two distinct forms, thick, garnet-red, lustrous prisms, or slender, golden-yellow, silky needles. Both of these forms melt at the same temperature, and can be converted the one into the other by recrystallisation. *Paranitrodiazoamidomesitylene* crystallises in golden-yellow, silky needles, and melts at 135—136° when rapidly heated, at 133° when slowly heated. *Paranitrodiphenylbuzylene*,  $NO_2 \cdot C_6H_4 \cdot N:N \cdot NH \cdot NHPh$ , is obtained by the action of phenylhydrazine on paranitrodiazo- or paranitroisodiazo-benzene nitrate, and crystallises from alcohol in dark, reddish-brown needles, but from light petroleum in small, orange-yellow needles, both forms melting at 104·5° (compare Curtius, *Abstr.*, 1893, i, 463).

Paranitrodiazoamidopiperidine has been previously described. The first product of the action of piperidine on the isodiazo-compound is the piperidine salt of *paranitroisodiazo-benzene hydroxide*, which crystallises in lemon-yellow plates, and melts and decomposes at 102—103°.

In the azo-series, the relations are not quite so simple. *Paranitrophenylazo- $\alpha$ -naphthylamine* and *paranitrophenylazodimethylaniline*, which have been previously described, may be prepared either from the normal- or iso-diazo-compound. *Paranitrophenylazo-diethylaniline* crystallises from benzene in dark, steel-blue, lustrous needles, and from alcohol in reddish-brown plates with a bronze lustre; both forms melt at 151°. *Paranitrophenylazodimethylorthotoluidine*, prepared from the normal compound, crystallises in brownish-red plates with a bronze lustre, and melts at 121–122°. It has not yet been found possible to prepare a crystalline colouring matter from *paranitroisodiazobenzene hydroxide*. *Paranitrophenylazomonomethylaniline*, prepared from the normal diazo-salt (Abstr., 1888, 271), forms orange-red needles or plates, melting at 133°. When prepared from *paranitroisodiazobenzene hydroxide*, however, the crystals, although identical in every other respect with those of the compound obtained from the normal diazo-salt, differ by having a golden-yellow colour. The two forms retain their characteristic colours on recrystallisation, but the orange-red compound yields a yellow product when it is dissolved in hydrochloric acid, the hydrochloride separated and decomposed by ice-cold ammonia, and the red, flocculent precipitate recrystallised three times. The nature of the relation between the two forms has not yet been ascertained. *Paranitrophenylazoethylaniline* exhibits similar relations. The colouring matter from the normal diazo-salt melts at 114–115° and crystallises in orange-red, lustrous needles, whilst the derivative of the isodiazo-compound forms golden-yellow needles of the same melting point. *Paranitrophenylazophenol* has been previously described, and may be obtained either from the normal- or the iso-diazo-compound.

The same is true of *paranitrophenylazo-orthocresol*, which forms yellowish-brown clusters melting at 200–201°, and of *paranitrophenylazometacresol*, which crystallises from toluene in violet-brown needles, with a bronze lustre, and from alcohol in long, orange-red, matted needles, melting at 162·5–163·5°.

$\alpha$ -Naphthol yields a mixture of two isomeric derivatives, both with the normal- and the iso-diazo-compound of *paranitraniline*. The  $\alpha$ -compound crystallises in dark brownish-red needles, which have a very pronounced, steel-blue, surface lustre; it melts at 277–279°, and decomposes at about 290°. The *sodium* salt forms greenish-brown needles with a bronze lustre. The isomeric  $\beta$ -compound forms long, brick-red, matted needles, which have a green, metallic lustre; it melts at 234–235° and decomposes at 255–260°. It is more soluble than the  $\alpha$ -compound in boiling amyl alcohol or xylene, by means of which the two forms may be separated. The *sodium* salt crystallises in greenish-black, matted needles. The  $\alpha$ -compound is always the chief product when the normal nitrodiazobenzene salt is used, whilst the proportion of the two forms obtained from the isodiazo-compound depends on the solvent employed, alcohol favouring the formation of the  $\alpha$ -compound, benzene that of the  $\beta$ -compound. Attempts to convert one of the compounds into the other have, so far, failed. The two compounds yield distinct acetates when heated with acetic

anhydride or chloride. The  $\alpha$ -acetate melts at 165—166°, and crystallises in ruby-red needles with a steel-blue surface lustre. The  $\beta$ -acetate crystallises in brick-red needles and melts at 179·5°.

The two isomeric compounds may also be prepared from paranitro-diazobenzene methyl ether, the  $\beta$ -compound being exclusively formed when benzene is used as the solvent, whilst, when alcohol is employed, the product consists entirely of the  $\alpha$ -compound.

$\beta$ -Naphthol only yields one azo-compound when treated either with the normal or the iso-diazo-derivative of paranitraniline. Similar isomeric derivatives have also been obtained from  $\alpha$ -naphthol by the action of the diazo-derivatives of paranitro-orthotoluidine. The  $\alpha$ -compound forms violet-brown needles, with a steel-blue surface lustre, melts indefinitely, and decomposes sharply at 247°. The acetate crystallises in dull, brown needles, melting at 163°. The  $\beta$ -compound forms dark brick-red, silky needles, and melts at 245°. When pressed on a porous plate, it exhibits a green, metallic lustre. The  $\beta$ -acetate crystallises in brick-red, lustrous needles melting at 172—173°.

A. H.

**Parethoxyazobenzene.** By ERNEST NAEGELI (*Bull. Soc. Chim.*, 1894, [3], 11, 897—898).—Parahydroxyazobenzene is heated with sodium ethoxide in alcoholic solution, and the solution of the sodium derivative thus formed boiled with ethylic iodide for some hours. On removing the solvent, a quantitative yield of *parethoxyazobenzene*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_5$ , is obtained in very long, orange needles, having a violet lustre; it melts at 85°, and boils at 325—326°. JN. W.

**Halogen Benzeneazophenols.** By JOHN T. HEWITT (*Ber.*, 1895, 28, 799—803).—The yellow 1 : 2- and the violet 1 : 3-chlorobenzeneazophenols previously described (*Abstr.*, 1894, i, 123) are not isomerides of the red and yellow varieties, but owe their different colour to the fact that they are crystallised with  $\frac{1}{2}\text{H}_2\text{O}$ . From 1 : 2-chlorobenzeneazophenol, the following derivatives were prepared (the numbers are melting points); *benzenesulphonate*, yellow prisms, 74°; *barium salt*, yellow needles, with  $4\text{H}_2\text{O}$ ; and the yellow *mononitroderivative*, 158°. From 1 : 3-chlorobenzeneazophenol were prepared the *benzenesulphonate*, yellow prisms, 97°, and the *barium salt*, orange needles, with  $4\text{H}_2\text{O}$ .

1 : 3-Bromobenzeneazophenol,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is obtained by treating 1 : 3-bromodiazobenzene hydrochloride with an alkaline solution of phenol; it crystallises from alcohol in yellow plates, from water in dark violet plates (containing  $\frac{1}{2}\text{H}_2\text{O}$ ). Derivatives: *acetate*, lustrous yellow plates, 112°; *benzoate*, orange needles, 122°; *sulphonate*, orange plates, 95°; *barium salt*, yellow needles, with  $4\text{H}_2\text{O}$ .

1 : 3-Chlorobenzeneazosalicylic acid is obtained by treating 1 : 3-chlorodiazobenzene hydrochloride with an alkaline solution of salicylic acid; it forms yellow spherical crystalline aggregates, melts at 220—221°, and has no tendency to crystallise with water. C. F. B.

**Action of Orthonitrobenzylic Chloride on Unsymmetrical Hydrazines.** By CARL PAAL and FRANZ FRITZ (*Ber.*, 1895, 28,

931—933; compare C. Paal and A. Bodewig, Abstr., 1892, 1455).—By acetylating compounds of the type  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NR}_2$ , the authors hoped to obtain derivatives which would condense to ring compounds of the type  $\text{N}=\text{CR}_2$   $\text{C}_6\text{H}_4\cdot\text{CH}_2$   $\text{>N}\cdot\text{NR}_2$ , but the basic properties of the open chain compounds proved too feeble.

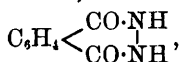
*Orthonitrobenzylidiphenylhydrazine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NPh}_2$ , from orthonitrobenzyl chloride and unsymmetrical diphenylhydrazine, crystallises from alcohol in red needles, and melts at  $143^\circ$ . It has no basic properties.

On attempting to prepare the corresponding methylphenylhydrazine derivative, the only product obtained was a very small amount of *orthonitrobenzylmethylaniline*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMePh}$ , which was probably formed from methylaniline, produced by oxidation of unchanged methylphenylhydrazine, as an identical compound was prepared from the former base. Orthonitrobenzylmethylaniline crystallises in large, resplendent, red needles; it melts at  $72^\circ$ , and decomposes when distilled. It is only slightly basic, but, on reduction, yields an unstable, oily base, probably the corresponding amido-compound. JN. W.

**$\alpha\beta$ -Diformylphenylhydrazine and  $\alpha\beta$ -Formylacetylphenylhydrazine.** By MARTIN FREUND and FRITZ HORST (*Ber.*, 1895, 28, 944—945).— $\alpha\beta$ -Diformylphenylhydrazine, is obtained by heating a mixture of phenylhydrazine and formic acid for seven hours. It crystallises from ether to which alcohol has been added, and melts at  $126^\circ$ . It is feebly acid in character, and is precipitated unchanged from the solution in dilute alkalis; it dissolves readily in cold formic acid, in hot water, and in warm, dilute alcohol, but is only sparingly soluble in cold water, ether, or benzene. When distilled, it undergoes decomposition, carbonic oxide, aniline, phenylic isocyanide, and  $\beta$ -formylphenylhydrazine being produced; the last-named substance is also formed when the diformyl derivative is treated with hot, aqueous ammonia.

$\alpha\beta$ -Formylacetylphenylhydrazine is obtained from  $\alpha\beta$  diformylphenylhydrazine by treatment with boiling acetic anhydride; it melts at  $86^\circ$ , and separates from hot water in long, colourless crystals containing water, but this is lost in the desiccator. This compound yields carbonic oxide when heated; the action of hot, aqueous soda gives rise to  $\beta$ -acetylphenylhydrazine. M. O. F.

**Action of Hydrazine Hydrate on Phthalic and Maleic Anhydrides.** By THEODOR CURTIUS and HANS A. FOERSTERLING (*J. pr. Chem.*, 1895, [2], 51, 371—398).—*Phthalylhydrazide*,



is prepared by adding hydrazine hydrate (1 mol.) to phthalic anhydride (1 mol.) dissolved in alcohol; the powder which separates is evaporated several times with water, and in this way the several compounds of which it consists are converted into the hydrazide. It crystal-



lises in slender, colourless needles, does not melt at  $340^{\circ}$ , can be sublimed at  $200^{\circ}$ , and distils at higher temperatures. One litre of boiling water dissolves 1 gram of it, and boiling alcohol dissolves it to some extent; otherwise it is insoluble. Its aqueous solution is acid, and it behaves as a monobasic acid, yielding easily soluble alkali salts, the solutions of which give precipitates with the salts of most of the heavy metals. The *potassium*,  $C_6H_4 < \begin{smallmatrix} CO \cdot NH \\ | \\ CO \cdot NK \end{smallmatrix}$  +  $4H_2O$ , *sodium*, *silver*,

*barium*,  $(C_6H_5O_2N_2)_2Ba + 2H_2O$ , and *calcium* derivatives are described. Phthalylhydrazide yields no derivative with benzaldehyde, and neither acids nor alkalis eliminate hydrazine from it; strong acids decompose it with formation of phthalic acid; bromine is without action on it. These facts show that the compound is not a hydrazine, as, indeed, is also evident from the fact that v. Rothenburg has prepared a hydrazine of this formula (Abstr., 1894, i, 285), and finds that it melts at  $250^{\circ}$ . The substance might contain the group  $< \begin{smallmatrix} NH \\ | \\ NH \end{smallmatrix}$  in place of one of the carbonyl-oxygen atoms of phthalic anhydride, but this possibility is negatived, since it yields no azo-compound on treatment with mercuric oxide, and does not split up with evolution of nitrogen and formation of phthalide when heated (compare Abstr., 1891, 1355).

*Diacetylphthalylhydrazide*,  $C_6H_4 < \begin{smallmatrix} CO \cdot N \cdot COMe \\ | \\ CO \cdot N \cdot COMe \end{smallmatrix}$ , is obtained when phthalylhydrazide is heated with excess of acetic anhydride; it forms crystals which melt at  $114^{\circ}$ .

*Methylphthalylhydrazide*,  $C_6H_4 < \begin{smallmatrix} CO \cdot NH \\ | \\ CO \cdot NMe \end{smallmatrix}$ , from the silver derivative and methylic iodide, melts at  $235^{\circ}$ .

*Ethylic phthalylhydrazide-acetate*,  $C_6H_4 < \begin{smallmatrix} CO \cdot NH \\ | \\ CO \cdot N \cdot CH_2 \cdot COOEt \end{smallmatrix}$ , is prepared by heating the anhydrous potassium derivative with ethylic chloracetate at  $160^{\circ}$ ; it crystallises in slender, yellowish needles, melts above  $300^{\circ}$ , and is sparingly soluble in hot water and alcohol. The corresponding *acid* closely resembles the ethylic salt, and may be regarded as a derivative of the still unknown hydrazineacetic acid (see this vol., i, 332), but attempts to isolate the latter from it have failed. The *ammonium* salt is described.

When an excess of hydrazine hydrate (2 mols.) is used in the preparation of phthalylhydrazide, *hydrazine phthalylhydrazide*,  $C_6H_4 < \begin{smallmatrix} CO \cdot NH \\ | \\ CO \cdot N \cdot N_2H_5 \end{smallmatrix}$ , is produced; this is a colourless, crystalline powder (sometimes with  $4H_2O$ ), and melts above  $270^{\circ}$ ; being a hydrazine salt, it yields benzylideneazine and phthalylhydrazide when its aqueous solution is shaken with benzaldehyde. Phenylhydrazine is without action on phthalylhydrazide.

Oxidising agents convert phthalylhydrazide into nitrogen and phthalic acid; reducing agents scarcely attack it.

Several compounds are formed when hydrazine hydrate and maleic

anhydride interact; after many recrystallisations, two, namely, *n*-amidomaleimide, and maleylhydrazide, were isolated in a pure condition.

*n*-Amidomaleimide,  $\text{CO} < \begin{smallmatrix} \text{C}_2\text{H}_2 \\ \text{O} \end{smallmatrix} > \text{C:N}\cdot\text{NH}_2$ , is a white powder which melts at  $111^\circ$ , and is insoluble in absolute alcohol, ether, and chloroform, but dissolves freely in water, from which, however, it cannot be recrystallised, for it yields a syrup when evaporated. The *silver* and *copper* derivatives were obtained as precipitates. When an aqueous solution of the imide is shaken with a few drops of benzaldehyde, crystals of a compound which has the properties of benzylideneazine separate, but no hydrazine is eliminated from the imide when it is heated with acetone for six hours.

Acetylamidomaleimide,  $\text{CO} < \begin{smallmatrix} \text{C}_2\text{H}_2 \\ \text{O} \end{smallmatrix} > \text{C:N}\cdot\text{NHAc}$ , crystallises when the imide is evaporated with glacial acetic acid on the water bath; it forms colourless needles, melts about  $280^\circ$ , and dissolves in water, alcohol, and glacial acetic acid. Methyl iodide has no action on amidomaleimide.

Maleylhydrazide,  $\text{C}_2\text{H}_2 < \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} >$ , forms small, white crystals, melts above  $250^\circ$ , and dissolves sparingly in hot alcohol, but more freely in hot water and glacial acetic acid. Its aqueous solution is strongly acid, and it closely resembles phthalylhydrazide in its behaviour to reagents.

*Hydrazine maleate*,  $\text{COOH}\cdot\text{C}_2\text{H}_2\cdot\text{COO}\cdot\text{N}_2\text{H}_5 + \text{H}_2\text{O}$  (compare Abstr., 1894, i, 348), is formed by the interaction of maleic acid (1 mol.) with hydrazine hydrate (1 mol.) in alcohol. It is a loose, white powder, melts at  $127^\circ$ , and is very soluble in water, giving an acid solution. Its conversion into 3 : 5 : 5-trimethylpyrazoline maleate,  $\text{C}_3\text{H}_3\text{N}_2\text{Me}_3\cdot\text{C}_2\text{H}_2(\text{COOH})_2$ , has been already described (*loc. cit.*).

*Hydrazine fumarate*,  $\text{COOH}\cdot\text{C}_2\text{H}_2\cdot\text{COO}\cdot\text{N}_2\text{H}_5 + 3\text{H}_2\text{O}$ , prepared in a similar manner, crystallises in small white needles; it melts at  $157^\circ$ , and dissolves readily in water, giving an acid solution, which yields a white precipitate with silver nitrate. It is not converted into trimethylpyrazoline fumarate when heated with acetone (compare *loc. cit.*).  
A. G. B.

**Symmetrical Trimethylbenzaldoxime.** By ARTHUR HANTZSCH and A. LUCAS (*Ber.*, 1895, **28**, 744—753).—Trimethylbenzanti-

aldoxime,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{C}\begin{smallmatrix} \text{H} \\ \parallel \\ \text{HO}\cdot\text{N} \end{smallmatrix}$ , has been previously prepared by Feith (Abstr., 1892, 329), it is not altered when boiled in aqueous or alkaline solution, and yields trimethylbenzonitrile by the action of hydrochloric acid, indicating its previous conversion into the syn-derivative. Under similar conditions, ordinary benzaldoxime also yields benzonitrile in small quantity. The *acetate* readily crystallises, melts at  $68^\circ$ , and regenerates the oxime when treated with sodium carbonate. The *synaldoxime*,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{C}\begin{smallmatrix} \text{H} \\ \parallel \\ \text{N}\cdot\text{OH} \end{smallmatrix}$ , is formed in small quantity together with

the anti-compound from which it is prepared by the action of hydrogen chloride; the anti-aldoxime hydrogen chloride is first formed, then the syn-compound, and by the further action of the gas a mixture of both; this regeneration of the anti-aldoxime is probably due to the presence of a little moisture. The compound crystallises in slender, colourless needles, melts at  $179^{\circ}$ , is more sparingly soluble than the anti-aldoxime, and yields no acetate. It is not altered when boiled with water, but with soda yields trimethylbenzonitrile which boils at  $235\text{--}238^{\circ}$ , not  $225\text{--}230^{\circ}$ , as stated by Küster and Stallberg (Abstr., 1894, i, 278). This is the first synaldoxime which has yielded a nitrile directly without previous conversion into the acetate. Phosphorus pentachloride converts aromatic oximes into nitriles, aliphatic oximes yield amides, trimethylbenzosynaldoxime yields the nitrile, but the anti-aldoxime gives some nitrile, the remainder undergoing intramolecular rearrangement (Beckmann's reaction) and yielding formylmesidide, dimolecular formylmesidide, and polymolecular formylmesidide.

*Formylmesidide*,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{NH}\cdot\text{CHO}$ , is formed in larger quantity at low temperatures when excess of the chloride is avoided; it is readily soluble in hot water, melts at  $176^{\circ}$ , and, by the action of hydrochloric acid, is resolved into formic acid and mesidine from which it is readily prepared. *Dimolecular formylmesidide chloride*,



or  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{NH}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , occurs together with the preceding compound from which it is readily prepared by the action of phosphorus pentachloride; it crystallises in lemon-yellow needles, melts at  $178^{\circ}$ , and is practically unaffected by boiling with water, ammonia, alkalis, or dilute acids. Its constitution is probably represented by the first of the above formulæ, as it is comparatively readily converted into formic acid and mesidine. *Dimolecular formylmesidide*,

$\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N} < \begin{smallmatrix} \text{CH}(\text{OH}) \\ \text{CH}(\text{OH}) \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , is prepared by boiling the preceding compound with alcohol, or by the action of concentrated sulphuric acid at ordinary temperatures; it melts at  $285^{\circ}$ , sublimes at higher temperatures, is very sparingly soluble, not acted on by aqueous or alcoholic acids and alkalis at  $100^{\circ}$ , but with concentrated hydrochloric acid at  $200^{\circ}$  it yields mesidine and formic acid. Its molecular weight and that of the chloride were determined by the cryoscopic method in benzene and phenol solution respectively. *Polymolecular formylmesidide* was only obtained in small quantity and was separated from the above chloride by taking advantage of its insolubility in benzene; it sublimes without melting, and is more stable and less soluble than the preceding compound, with which it is polymeric or isomeric, as it yields the same products when hydrolysed.

J. B. T.

**Action of Acetanilide on Mercuric Acetate.** By LEONE PESCI (*Gazzetta*, 1894, 24, ii, 449—452).—*Paramercuriodiphenylenediacetylmercuriodiammonium acetate*,  $\text{Hg} < \begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{NHAc} \\ \text{C}_6\text{H}_4\cdot\text{NHAc} \end{smallmatrix} \text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ , is pre-

pared by gradually adding mercuric acetate to a boiling aqueous solution of acetanilide and heating the solution until caustic potash gives a pure white precipitate; the salt, which separates on cooling, crystallises in lustrous rhombs melting at  $218-220^{\circ}$ . The corresponding *chloride* crystallises with  $2\text{H}_2\text{O}$  in colourless needles melting at  $256^{\circ}$ , whilst the *sulphate* forms colourless needles or laminae which, on heating, decompose without melting. The *hydroxide* is a micro-crystalline substance having a strongly alkaline reaction; it decomposes at  $270^{\circ}$ , and when treated with sodium sulphide or barium sulphide loses mercury yielding *paramercurioacetanilide*,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHAc})_2$ . This substance crystallises in colourless, flexible needles melting at  $244-246^{\circ}$ , and when heated with alcoholic potash in a closed tube yields paramercurioaniline, showing that in the above compounds the mercury occupies the para-position relatively to the amidogen residue in the aromatic nucleus. W. J. P.

**Mercurioacetanilides.** By ANTONIO PICCININI (*Gazzetta*, 1894, **24**, ii, 453—457).—The mercurioacetanilide prepared by Pesci (see preceding abstract) is isomeric with the substance obtained by Oppenheim and Pfaff (*Ber.*, 1874, **7**, 624) by the action of yellow mercuric oxide on fused acetanilide, to which the constitution  $\text{Hg}(\text{NAcPh})_2$  was assigned. The latter substance is decomposed by sodium thiosulphate, potassium iodide, or ammonium bromide, yielding acetanilide in accordance with the general reactions of mercurammonium compounds; Pesci's compound, on the other hand, is not changed by these reagents. W. J. P.

**Organo-mercuric Compounds derived from Aniline.** By ANTONIO PICCININI (*Gazzetta*, 1894, **24**, ii, 457—465).—Paramercuriodiphenylenemercuriodiammonium acetate is converted into paramercurioaniline by sodium thiosulphate; whilst if warmed with potassium iodide solution, it yields *paramercurioaniline iodide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgI}$ , probably as a product of the action of mercuric iodide on paramercurioaniline produced in the first stage of the action. The iodide crystallises in colourless laminae melting and decomposing at  $165^{\circ}$ . The corresponding *bromide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgBr}$ , is formed by the action of ammonium bromide on the acetate mentioned above; it crystallises in colourless laminae melting at  $182^{\circ}$ .

Paramercuriodiphenylenedimethylmercuriodiammonium acetate is converted into paramercuriomethylaniline by sodium thiosulphate, and into *paramercuriomethylaniline bromide* by ammonium bromide; this salt crystallises in colourless needles melting and decomposing at  $164^{\circ}$ .

Paramercuriodiphenylenetetramethylmercuriodiammonium acetate gives mercuriodimethylaniline with sodium thiosulphate and the *iodide*  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgI}$  of the latter base with potassium iodide; the iodide crystallises in needles or scales melting and decomposing at  $174-195^{\circ}$ . The corresponding *bromide* is obtained by acting on the acetate of the substituted ammonium with ammonium bromide; it crystallises in lustrous, colourless scales melting and decomposing at  $195^{\circ}$ .

Paramercuriodiphenylenediethylmercuriodiammonium acetate is converted into mercurioethylaniline by sodium thiosulphate, and by potassium iodide into the *iodide*  $\text{NHEt}\cdot\text{C}_6\text{H}_4\cdot\text{HgI}$ , crystallising in colourless needles melting at  $137^\circ$ .

Paramercuriodiphenylenetetrethylmercuriodiammonium acetate, under similar conditions, yields paramercuriodiethylaniline; its *iodide*,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgI}$ , crystallises in colourless needles melting at  $120^\circ$ , and its *bromide* in colourless needles melting at  $154.5^\circ$ .

All these ammonium derivatives thus behave in a similar and characteristic manner with sodium thiosulphate, potassium iodide and ammonium bromide respectively. W. J. P.

**Paramercuriodiethylaniline.** By PIO PIGORINI (*Gazzetta*, 1894, 24, ii, 465—468).—*Mercuriodiethylaniline chloride*,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ , is obtained from paramercuriodiethylaniline by the process used by Michaelis and Rabinerson (*Abstr.*, 1890, 1269) in preparing mercurio-dimethylaniline chloride; it crystallises in colourless needles melting at  $164^\circ$ . On heating with sodium carbonate solution, it yields the *oxide*  $\text{O}(\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2)_2$ ; this is a substance having a strongly alkaline reaction and crystallises in lustrous, colourless needles melting at  $220^\circ$ ; it yields paramercuriodiethylaniline on treatment with sodium thiosulphate. W. J. P.

**Paraphenetoilcarbamide, "Dulcin."** By LUDWIG WENGHÖFFER (*Chem. Centr.*, 1894, i, 771—773; from *Apoth. Ztg.*, 9, 200—202).—*Paraphenetoilcarbamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , is obtained by gradually adding a solution of paraphenetidine in benzene or toluene to a 20 per cent. solution of carbonyl chloride in benzene or toluene, whereby paraphenetidinecarbonyl chloride,  $\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , is formed; after remaining from half an hour to one hour, the mixture is filtered and the filtrate treated with ammonia gas or shaken with a strong solution of ammonia. The ammonium chloride which is precipitated is filtered off and the filtrate evaporated; the residue is washed with cold water and crystallised from boiling water. If concentrated solutions are employed in the above reaction, diparaphenetoilcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , is also formed. According to F. v. Heyden, when large quantities of the above reagents are employed, paraphenetidinecarbonyl chloride is not formed, or only in small quantities; but the reaction takes place with the formation of paraethoxyphenylic isocyanate,  $\text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , which when treated with ammonia yields paraphenetoilcarbamide.

Paraethoxyphenylic isocyanate is easily obtained by passing carbonyl chloride over melted paraphenetidine hydrochloride, or by heating paraphenetidine with carbonyl chloride at  $230^\circ$ . It is also obtained by passing carbonyl chloride over diparaphenetoilcarbamide heated at  $230^\circ$ .

Paraphenetoilcarbamide is obtained in small quantities by the action of carbamide on paraphenetidine. A good yield is, however, obtained when paraphenetidine hydrochloride is fused with carbamide; at the same time, when excess of carbamide is employed, diparaphenetoilcarbamide is formed, which, however, is easily converted

into paraphenetoilcarbamide by heating it with an equivalent quantity of carbamide in a closed vessel at 150—160°.

Paraphenetoilcarbamide is likewise obtained by heating paraphenetidine with acetylcarbamide, carbamine chloride or urethane. It forms colourless crystals, melts at 173—174°, is soluble in 800 parts of water at 15°, in 50 parts of boiling water, and in 25 parts of 90 per cent. alcohol. When boiled with water, it is gradually decomposed into diparaphenetoilcarbamide and ammonium carbonate. It dissolves completely and without any coloration in concentrated sulphuric acid, and has no injurious action on the animal organism. It can be detected by the following reaction: a small quantity is boiled with two or three drops of pure carbolic acid and sulphuric acid, then somewhat diluted with water, and to the cold solution a solution of sodium hydroxide or ammonia is added, when a blue coloration is formed at the junction of the two liquids.

E. C. R.

**Benzanilide.** By ERNEST NAEGELI (*Bull. Soc. Chim.*, 1894, [3], 11, 891—893).—Improved methods of preparation. Benzoic chloride is added to excess of aniline (10 mols.) at 30—40°, and the mixture heated at 60—70° for half an hour. The excess of aniline is then dissolved out with dilute hydrochloric acid, leaving a quantitative yield of an almost white product.

A 90 per cent. yield of a less pure product may be obtained from the acid. This is melted in a retort, and the aniline (1 mol.), heated to about the same temperature, added; the temperature is then repeatedly raised from 180° to 225° during about 30 hours, the loss of aniline being made up from time to time. The cold product, after washing with dilute alkali and acid, is fairly pure; the colour, however, is violet-grey, and the alcoholic solution shows a strong violet-brown fluorescence. Further purification may be effected by sublimation.

J. N. W.

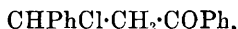
**Action of Phthalic Chloride on Nitranilines.** By N. DOBREFF (*Ber.*, 1895, 28, 939—941; compare Pawlewski, this vol., i, 134).—Paranitrophthalanil is obtained by heating paranitraniline with phthalic chloride; it crystallises from alcohol in yellowish needles and melts at 190—190.5° (compare *loc. cit.*). The solution in alkalis and alkali carbonates is yellow. Metanitrophthalanil crystallises from alcohol and melts at 236—236.5°.

M. O. F.

**Phenyl Derivatives of Glycolaldehyde.** By CÆSAR POMERANZ (*Monatsh.*, 1894, 15, 739—746).—The acetal of the phenyl derivative of glycolaldehyde, *phenoxyacetal*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , is obtained on heating an alcoholic solution of sodium phenoxide and monochloroacetal for eight hours at 200°. It boils at 257°, and when heated with dilute sulphuric acid and subsequently distilled in a current of steam, forms the hydrate of the phenyl derivative of glycolaldehyde, *phenoxyacetaldehyde*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{COH} + \text{H}_2\text{O}$ . This melts at 38°, has an aromatic odour, reduces silver solution, is converted by silver oxide

into phenoxyacetic acid, and, on distillation under reduced pressure, loses water and yields the aldehyde; this boils at 118—119° (30 mm.), and after remaining some days changes to a jelly-like mass. It yields a *hydrazone*,  $C_{14}H_{14}N_2O$ , which crystallises from alcohol in bright, yellow prisms and melts at 86°. The corresponding *oxime*,  $C_8H_9O_2N$ , crystallises from light petroleum in prisms, melts at 95°, and when warmed with acetic anhydride yields *phenoxyacetoneitrile*,  $OPh \cdot CH_2 \cdot CN$ , which boils at 239—240°. G. T. M.

**$\beta$ -Halogenised Ketones.** By HANS RUPE and FELIX SCHNEIDER (*Ber.*, 1895, **28**, 957—966).— $\beta$ -Chloro-*o*-benzylacetophenone,



was first obtained by Claisen and Claparède on submitting a mixture of benzaldehyde with acetophenone to the action of hydrogen chloride. When it is heated with phenylhydrazine (2 mols.), triphenylpyrazoline is formed. The *bromo*-derivative crystallises in nacreous leaflets and melts at 111°.

$\beta$ -Thiocyano-*o*-benzylacetophenone,  $SNC \cdot CHPh \cdot CH_2 \cdot C(=O)Ph$ , is obtained by heating an alcoholic solution of the chloro-ketone for several hours with potassium thiocyanate. It melts at 88—89°, and undergoes no change when heated on the water bath; the solutions in organic solvents exhibit a bright blue fluorescence. Unlike most compounds of this class, it does not yield a hydroxythiazole derivative under the influence of condensing agents. When heated with phenylhydrazine, it gives rise to triphenylpyrazoline.

$\beta$ -Cyano-*o*-benzylacetophenone, or  $\alpha$ -phenyl- $\beta$ -benzoylpropionitrile,  $CN \cdot CHPh \cdot CH_2 \cdot C(=O)Ph$ , which melts at 127°, is prepared by heating an alcoholic solution of the chloro-ketone with potassium cyanide for half an hour in a reflux apparatus; if the liquid is cooled immediately after the first separation of potassium chloride, benzylideneacetophenone is the chief product. A compound,  $C_{31}H_{24}NO$ , is also formed in varying quantity; it dissolves with difficulty in most solvents, but crystallises from boiling glacial acetic acid in slender, white needles and melts at 249°.

$\alpha$ -Phenyl- $\beta$ -benzoylpropionic acid crystallises from alcohol in white needles and melts at 153°. The *methylic* salt melts at 104°, the *ethylic* salt at 37—38°, and the *amide* at 149°. The *anhydride* of the phenylhydrazone,  $C_{22}H_{18}N_2O$ , crystallises from ether in stellar aggregates, and melts at 122—123°.

Chlorobenzylacetophenone yields a compound which melts at 155° when heated with aniline; paratoluidine gives rise to a compound,  $C_6H_4Me \cdot NH \cdot CHPh \cdot CH_2 \cdot C(=O)Ph$ , which melts at 166.5°, and forms a *bromo*-derivative melting at 100.5°.

*Benzylideneacetophenoneoxime* crystallises in white needles and melts at 107—108°; the *bromo*-derivative melts at 152°. An isomeride is formed when the alcoholic solution of  $\beta$ -chloro-*o*-benzylacetophenone is heated with aqueous hydroxylamine for an hour and a half on the water bath; it crystallises in white needles and melts at 73°. It does not form a *bromo*-derivative, and it also differs from the isomeric substance in its behaviour towards hot, dilute acids, which are with-

out action on it. This is due to the fact that 1 mol. of hydrogen chloride has been removed from the oxime of  $\beta$ -chloro- $\omega$ -benzylacetophenone, giving rise to *diphenyldihydroisoxazole*,  $\text{CHPh} \begin{smallmatrix} \text{O} \cdot \text{N} \\ \text{CH}_2 \end{smallmatrix} \text{CPh}$  (compare Abstr., 1892, 992). A compound, which melts at  $190^\circ$ , is formed at the same time; it yields a bromo-derivative which melts at  $95^\circ$ .  
M. O. F.

**Thio-Derivatives of Ketones.** By EUGEN BAUMANN and EMIL FROMM (*Ber.*, 1895, **28**, 895—907).—It has been previously shown (*Ber.*, **22**, 1035 and 2592) that acetone and hydrogen sulphide only react in presence of some condensing agent such as hydrogen chloride or zinc chloride; ethyl methyl ketone, diethyl ketone, ethylic acetoacetate, pinacone, acetophenone, methyl hexyl ketone, quindecyl methyl ketone, and metadihydroxybenzophenone all resemble acetone in this respect, but the last three compounds do not react even in presence of a condensing agent. The ketones thus present a marked contrast to the aldehydes, most of which readily combine with hydrogen sulphide. The ketones which react yield only one trithio-derivative instead of the two stereoisomerides which are indicated by theory, and E. Wörner has recently shown that none of the aromatic hydroxy- and benzoyl-aldehydes form isomeric trithio-compounds, but that the corresponding alkyloxy-aldehydes follow the general rule and yield the two stereoisomerides.

Acetophenone and hydrogen sulphide, in presence of hydrogen chloride, give four compounds—thioacetophenone, trithioacetophenone, anhydrotriacetophenone bisulphide, and a green, resinous compound, containing oxygen and sulphur.

*Thioacetophenone*,  $\text{S} \cdot \text{CPhMe}$ , is the first product of the action, and is most readily obtained by the rapid distillation of trithioacetophenone; it is also formed in small quantity by the interaction of alcoholic hydrochloric acid and trithioacetophenone at  $30$ — $40^\circ$ ; at lower temperatures the reverse change occurs. It is a blue, oily liquid with a smell of garlic; the colour of its vapour resembles that of iodine, it is rapidly decomposed by water, and yields a mixture of cinnamene and ethylbenzene when boiled.

*Trithioacetophenone*,  $\text{S} \begin{smallmatrix} \text{C}(\text{MePh}) \cdot \text{S} \\ \text{C}(\text{MePh}) \cdot \text{S} \end{smallmatrix} \text{CMePh}$ , which is most readily formed at  $0^\circ$ , crystallises from alcohol in needles, and melts at  $122^\circ$ . It is not volatile with steam, is not decomposed by alcoholic potash, has no smell, and, in alcoholic solution, is not affected by a trace of iodine. All attempts to prepare an isomeric compound were fruitless. The molecular weight was determined cryoscopically. The principal compound formed by the action of ammonium sulphide on acetophenone in alcoholic solution is not "polymeric thioacetophenone" (m. p.  $119.5^\circ$ ), as stated by Engler (*Ber.*, **11**, 930), but  *$\alpha$ -phenylethyllic bisulphide*,  $\text{S}_2(\text{CHPhMe})_2$  (compare following abstract).

The residue obtained by the distillation of trithioacetophenone or of thioacetophenone, consists of 2 : 5- and 2 : 4-diphenylthiophen (this vol., i, 337). *Anhydrotriacetophenone bisulphide*,  $\text{S} \begin{smallmatrix} \text{C}(\text{MePh}) - \text{S} \\ \text{C}(\text{MePh}) \text{CH} \end{smallmatrix} \text{CPh}$



or  $\text{CMePh} \begin{smallmatrix} \text{S} \\ \text{<} \end{smallmatrix} \text{CPh} \cdot \text{CH} \cdot \text{CMePh}$ , is formed together with the trithio-compound, but is deposited more slowly; it crystallises in needles, melts at  $107\text{--}108^\circ$ , and, at  $180^\circ$ , yields thioacetophenone, hydrogen sulphide, and 2 : 4-diphenylthiophen only (*loc. cit.*). It is not formed from trithioacetophenone by the action of alcoholic hydrogen chloride, but is probably derived from labile *cis*-trithioacetophenone, as indicated by the first formula. The molecular weight was determined in naphthalene solution. The resinous compound is formed during the preparation of trithioacetophenone if the temperature rises or if the solution is too concentrated; when distilled, it yields thioacetophenone, cinnamene, hydrogen sulphide, and 2 : 4-diphenylthiophen only, so that it is probably a mixture of anhydrotriacetophenone bisulphide with acetophenone condensation products. J. B. T.

**Action of Ammonium Sulphide on Acetophenone.** By EUGEN BAUMANN and EMIL FROMM (*Ber.*, 1895, **28**, 907—914).—Acetophenone reacts like benzophenone with ammonium sulphide in alcoholic (65 per cent.) solution at ordinary temperatures, and yields *α*-phenylethylic bisulphide,  $\text{S}_2(\text{CHMePh})_2$ , not “polymeric thioacetophenone,” as stated by Engler; it crystallises in small, colourless prisms, and melts at  $57\text{--}58^\circ$ ; its molecular weight agrees with the formula, and its constitution is shown by its reduction to *α*-phenylethylic mercaptan,  $\text{CHMePh} \cdot \text{SH}$ , which boils at  $119\text{--}200^\circ$ , and gives the ordinary mercaptan reactions. The bisulphide, when heated, is readily resolved into cinnamene, a little ethylbenzene, sulphur, and hydrogen sulphide; the residue consists of sulphur, 2 : 5- and 2 : 4-diphenylthiophen (compare this vol., i, 337); the first few drops of the distillate are blue, and contain a trace of thioacetophenone. In addition to the above bisulphide, an oily compound is formed; it is practically free from thioacetophenone, commences to decompose at  $160^\circ$ , and, when further heated, evolves hydrogen sulphide, and yields ethylbenzene and a little cinnamene; the residue contains sulphur, and 2 : 5- and 2 : 4-diphenylthiophen. With stronger alcohol, and operating exactly as Engler describes, crystals of ammonium hydrogen sulphide are deposited; the oil obtained by precipitation with water, yields, when distilled, ethylic sulphide, ethylic alcohol, cinnamene, ethylbenzene, thioacetophenone (traces), acetophenone, 2 : 5- and 2 : 4-diphenylthiophen, sulphur, and hydrogen sulphide; the residue consists of resinous matter and sulphur. In explanation of the difference between these results and Engler's, the authors suggest that his “polymeric thioacetophenone” (m. p.  $119^\circ$ ) was 2 : 4-diphenylthiophen; the melting points and general properties agree tolerably well; the difference in composition was probably due to the presence of free sulphur in Engler's compound, which does not greatly affect the melting point, and is extremely difficult to separate. J. B. T.

**Diphenylamine-*n*-oxychlorophosphine.** By PAUL OTTO (*Ber.*, 1895, **28**, 613—616).—When diphenylamine (1 mol.) is heated for 12 hours at  $160^\circ$  with phosphorus oxychloride (2 mols.) *diphenylamine-*n*-oxychlorophosphine*,  $\text{NPh}_2 \cdot \text{POCl}_2$ , is formed. This crystallises in

white plates and melts at  $57^{\circ}$ . With water, it yields the *phosphinic acid*,  $\text{NPh}_2\cdot\text{PO}(\text{OH})_2$ , which is itself unstable, but the *ethylic*, *phenylic*, and 1 : 4-*tolyl*ic salts of which,  $\text{NPh}_2\cdot\text{PO}(\text{OEt})_2$ , &c., can be obtained respectively by boiling the chlorophosphine with alcohol or heating it with phenol or 1 : 4-cresol in sealed tubes; they are white substances, and melt at  $175^{\circ}$ ,  $180^{\circ}$ , and  $178^{\circ}$ . When the chlorophosphine (1 mol.) is heated with aniline, 1 : 2-toluidine, or piperidine (4 mols.), *diphenylaminedianiline-n-phosphine oxide*,  $\text{NPh}_2\cdot\text{PO}(\text{NPh})_2$ , or the corresponding *di*-1 : 2-toluidine, or *dipiperidine*, compounds, are respectively formed; these are white, and melt at  $232^{\circ}$ ,  $219^{\circ}$ , and  $200^{\circ}$ .

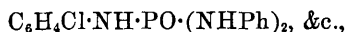
C. F. B.

**1 : 4-Chloraniline-n-oxychlorophosphine.** By PAUL OTTO (*Ber.*, 1895, **28**, 616—620).—When phosphorous oxychloride (2 mols.) is heated with 1 : 4-chloraniline hydrochloride (1 mol.), 1 : 4-chloraniline-n-oxychlorophosphine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{POCl}_2$ , is formed; it crystallises in white needles, and melts at  $107^{\circ}$ . When it is dissolved in ammonia, and the solution acidified with hydrochloric acid, the *phosphinic acid*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{PO}(\text{OH})_2$ , is formed; this crystallises in white, silky needles, and melts at  $155^{\circ}$ ; the colourless *ethylic salt* melts at  $76^{\circ}$ , the yellowish *phenylic salt* at  $117^{\circ}$ .

When phosphorus oxychloride (1 mol.) is heated with 1 : 4-chloraniline hydrochloride (2 mols.) a waxy mass is obtained, from which *di*-1 : 4-chloraniline-n-phosphinic acid,  $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH})_2\text{PO}\cdot\text{OH}$ , can be isolated; it crystallises in silvery white plates, and melts at  $126^{\circ}$ . If the waxy mass is heated over a bare flame, a violent evolution of hydrogen chloride occurs, and *oxyphosphazo*-1 : 4-chlorobenzenechloranilide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{PO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ , is formed; this crystallises in white needles, and melts above  $300^{\circ}$ , as does also its yellow *dinitro-derivative*.

When phosphorus oxychloride (1 mol.) is heated with 1 : 4-chloraniline (6 mols.), the *phosphine oxide*,  $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH})_3\text{PO}$ , is formed; this crystallises in white plates, and melts at  $230^{\circ}$ ; its yellow *trinitro*- and white *tribromo-derivatives* melt respectively at  $249^{\circ}$  and  $236^{\circ}$ .

1 : 4-Chloraniline-n-oxychlorophosphine reacts with aniline, 1 : 2-toluidine and piperidine, yielding mixed phosphine oxides,



which crystallise in white plates, and melt respectively at  $115^{\circ}$ ,  $150^{\circ}$ , and  $175^{\circ}$ .

C. F. B.

**Nitrobenzoic acids: An omission.** By WILLIAM OECHSNER DE CONINCK (*Bull. Soc. Chim.*, 1894, [3], **11**, 717; compare this vol., i, 280).—The nitrobenzoic acids, taken in pairs, bear the same relations to each other as do the amidobenzoic acids. JN. W.

**Derivatives of Cinnamic acid.** By LAZAR EDELEANU and A. ZAHARIA (*Chem. Centr.*, 1894, ii, 208—209; from *Bul. Soc. Sci. fizice*, Bucharest, **3**, 80—86).—The following substances have been obtained by agitating amines or phenols with cinnamic chloride in the presence of potash, and crystallising the product from alcohol.

*Cinnamoylpariodaniline*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{I}$  [1:4], melting at  $204^\circ$ , sparingly soluble in alcohol. *Cinnamoylorthotoluidine*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , melting at  $167^\circ$ . *Cinnamoylparatoluidine*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}$ , melting at  $168^\circ$ . *Cinnamoylparaxylidine*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$  [ $\text{NH}:\text{Me}_2$ , 1:3:4], melting at  $175\text{--}176^\circ$ . *Cinnamoylmetaxylidine*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$  [ $\text{NH}:\text{Me}_2$ , 1:3:5].

Dibromocinnamic chloride reacts violently with ammonia and with aniline; in the former instance *dibromocinnamamide*,



is formed; it crystallises from alcohol, in which it is very sparingly soluble, in needles with silky lustre, and melts at  $217^\circ$ . In the latter case, a crystalline substance, readily soluble in alcohol, and dibromocinnamylanilide, melting at  $174^\circ$ , are produced. With methylaniline and dimethylaniline, cinnamic chloride, in alkaline emulsion, yields cinnamic anhydride. Cinnamic chloride does not react with secondary and tertiary amines; with phenols, the action is much less vigorous than with the amines, and it is frequently advantageous to omit the potash with phenols. *Orthotolylic cinnamate*, m. p.  $85^\circ$ , has been obtained from orthocresol, *paratolylic cinnamate*, m. p.  $60^\circ$ , from paracresol and similarly, from catechol, a salt melting at  $125^\circ$ ; from resorcinol, a salt melting at  $113\text{--}114^\circ$ ; from quinol, a salt melting at  $186\text{--}187^\circ$ ; and from  $\alpha$ -naphtol, a salt melting at  $111^\circ$ .

D. A. L.

**Thionyl Compounds of some Aromatic Ethylic Salts.** By ALFRED HERRE (*Ber.*, 1895, **28**, 593—600).—These compounds have been prepared by heating ethylic salts of aromatic amido-acids with thionyl chloride in benzene solution. The presence of hydroxyl in the benzene ring hinders the formation of a thionylamine; for example, ethylic amidosalicylate yields no thionylamine; ethylic amidoanisate does, however. Ethylic 1:2-amidocinnamate yields carbostyryl. The temperatures given below, except where otherwise indicated, are melting points.

*Ethylic 4-amidocinnamate*, yellow needles,  $68\text{--}69^\circ$ ; the *thionyl derivative*,  $\text{SO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COOEt}$ , yellow needles or plates,  $95^\circ$ ; it boils at  $235\text{--}240^\circ$  under 90—100 mm. pressure. *Ethylic 3:5-nitroamidobenzoate*, prepared by reducing the dinitro-salt with ammonium sulphide, yellow needles,  $155^\circ$ ; *thionyl derivative*, lustrous yellow plates,  $48\text{--}49^\circ$ . *Methylic 3:5-dinitrobenzoate*, colourless prisms and plates,  $112^\circ$ ; when reduced with ammonium sulphide it yields the *nitramidobenzoate*, yellow needles,  $160^\circ$ ; the *thionyl derivative* of the latter, yellow crystals,  $55\text{--}56^\circ$ . *Ethylic 4-amidotoluete*, by reducing the corresponding nitro-compound with alcoholic ammonium sulphide; colourless needles,  $79^\circ$ ; *thionyl derivative*, yellow crystals,  $14\text{--}15^\circ$ . *Methylic 4-nitrotoluete*, needles,  $72^\circ$ ; *amidotoluete*, white prisms,  $115^\circ$ ; *thionyl derivative* of the latter, yellow plates,  $94^\circ$ . *Ethylic 3-amidosalicylate*, by reducing the nitro-compound with iron and hydrochloric acid, forms white needles which darken when exposed to air, and melts at  $145^\circ$ . *Ethylic thionyl-3-amidoanisate*, yellow prisms, melting at  $45^\circ$ .

C. F. B.

**Isomerism of Ethylic Formylphenylacetate.** By WILHELM WISLICENUS (*Ber.*, 1895, 28, 767—774).—The isomerism of the two ethylic formylphenylacetates,  $\text{CHO}\cdot\text{CHPh}\cdot\text{COOEt}$ , previously described by the author (*Abstr.*, 1887, 129), is similar to that observed by Claisen in the hydroxymethylene- (formyl-) derivatives and the 1:3-diketones. Of the dibenzoylacetones, the more acid one reacts with ferric chloride, and is formed from the other by the action of sodium ethoxide. The ethylic formylphenylacetates show the opposite behaviour, the liquid isomeride alone reacts with ferric chloride, is sparingly soluble in alkalis, and is readily converted by them into the solid compound. Both substances appear to yield identical copper salts, and they have the same molecular weight. On the assumption of their tautomerism they have the formulæ  $\text{CHO}\cdot\text{CHPh}\cdot\text{COOEt}$  and  $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$ , the latter represents the solid acid compound, the former the liquid isomeride, and their behaviour is in accord with Perkin's observations that the keto-form predominates as the temperature rises. Too little is known of the ferric chloride reaction, for this to serve as an argument against these formulæ. The compounds may be stereoisomeric,  $\begin{array}{c} \text{H}\cdot\text{C}\cdot\text{OH} \\ | \\ \text{Ph}\cdot\text{C}\cdot\text{COOEt} \end{array}$  and  $\begin{array}{c} \text{H}\cdot\text{C}\cdot\text{OH} \\ | \\ \text{COOEt}\cdot\text{C}\cdot\text{Ph} \end{array}$ ; in this case, three substances are possible, but it is probable that only one form might be capable of existence. Each isomeride slowly changes into the other at ordinary temperatures, apparently until equilibrium is established, but the solid is more readily produced at low, the liquid at high, temperatures. With phenylhydrazine in alcoholic or ethereal solution, at ordinary temperatures, both isomerides yield a *phenylhydrazone*,  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2$ , which is deposited in colourless crystals, melts at 63—64°, gives a dark cherry colour with concentrated sulphuric acid, and a dark brown coloration with ferric chloride. When heated at 180°, or by the action of hydrogen chloride, it is converted into 1:4-diphenylpyrazolone (m. p. 195—196°). From the mother liquor, two compounds are deposited in small quantity, the one in yellow prisms, the other in small yellow needles; they contain nitrogen, and melt at 91—93° and 155—156° respectively. The former is probably the *phenylhydrazide*,  $\text{CHO}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ .

J. B. T.

**Behaviour of the Calcium Salts of Alkyl Derivatives of Aromatic Acids on dry Distillation.** By EDUARD HÜBNER (*Monatsh.*, 1894, 15, 719—738; compare Arnstein, *Abstr.*, 1894, i, 527).—When calcium metamethoxybenzoate is submitted to dry distillation, it yields anisole, phenol, and methylic metamethoxybenzoate, which boils at 236—238°. Calcium methylsalicylate gives anisole, phenol, methylsalicylic acid and methylic methylsalicylate.  $\beta$ -Creosotic acid (orthohomosalicic acid) [ $\text{COOH}:\text{OH}:\text{Me} = 1:2:3$ ] melts at 163—164°, and forms the following derivatives. A *calcium salt*, which crystallises with  $2\text{H}_2\text{O}$ ; a *barium salt*, which crystallises with  $3\text{H}_2\text{O}$ ; a *methylic salt*, which boils at 232—233°; and an *ethylic salt*, which boils at 242—243°. On heating the methylic salt with potash and methylic iodide, the compound  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{COOMe}$  is formed. It boils at 241—242°, and on hydrolysis yields the acid



which melts at  $85^{\circ}$ , yields a *barium salt*, crystallising with  $3\frac{1}{2}\text{H}_2\text{O}$ , and a *calcium salt*, which, on dry distillation, gives orthocresol, the methyl derivative of orthocresol and methylic orthomethoxymetatonate. Methoxynaphthoic acid [ $\text{OMe} : \text{COOH} = \alpha : \beta$ ] melts at  $127^{\circ}$ ; it is prepared from the methylic salt, which boils at  $223\text{--}225^{\circ}$  (60 mm.). The calcium salt, on dry distillation, yields  $\alpha$ -naphthol and the methyl derivative of naphthol, but does not appear to form the methylic salt of naphthoic acid. G. T. M.

**Formation of Veratric acid from Hemipinic acid.** By CARL KÜHN (*Ber.*, 1895, 28, 809—811).—*Amidoveratric acid* (dimethoxyanthranilic acid),  $\text{NH}_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{COOH}$ , is formed when hemipinimide is treated with alkaline sodium hypochlorite. It crystallises in colourless needles, melts at  $181\text{--}183^{\circ}$ , and is soluble in dilute alkalis and acids. The *hydrochloride* crystallises in needles. The *acetyl*-derivative also forms colourless needles, and melts at  $188\text{--}190^{\circ}$ . When treated with an alcoholic solution of amyl nitrite and sulphuric acid, the free acid is converted into veratric acid, the yield amounting to 43 per cent. A. H.

**Glyoxylic acid.** By CARL BOETTINGER (*Arch. Pharm.*, 1894, 232, 704—718; and 1895, 233, 100—104).—With phenols, glyoxylic acid forms condensation products of, as yet, uncertain constitution. These compounds give precipitates with a solution of gum.

$\alpha$ -*Diresorcinolacetic acid*,  $\text{C}_{14}\text{H}_{12}\text{O}_6$ , has already been obtained by Causse, who, however, on insufficient evidence, considered it to have the formula  $\text{COOH}\cdot\text{CH}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ . It crystallises in needles which give off vapour at  $240^{\circ}$  and melt to a clear oil. It yields an *acetyl derivative* melting at  $138^{\circ}$ , which is probably the triacetyl derivative  $\text{C}_{14}\text{H}_7\text{O}_6(\text{C}_2\text{H}_3\text{O})_3$ , but may be a diacetyl derivative.

$\beta$ -*Diresorcinolacetic acid* is formed at the same time as the  $\alpha$ -compound; it is a brittle, white mass, easily soluble in cold water. Its salts resemble those of the  $\alpha$ -acid. It reacts readily in the cold with acetic anhydride, and forms the same acetyl derivative as the  $\alpha$ -compound.

$\beta$ -*Dicatecholacetic acid* forms a yellow, hygroscopic, glass-like substance. It yields a *triacetyl derivative*.

$\beta$ -*Dipyrogallolacetic acid* is very easily obtained. It forms a hygroscopic, white mass, which loses 3 mols. of water at  $100^{\circ}$ . When an alkali is added to a solution of the acid, a very intense and characteristic blue coloration is produced. It yields a *triacetyl derivative*,  $\text{C}_{14}\text{H}_7\text{O}_6(\text{C}_2\text{H}_3\text{O})_3$ , which melts at  $123^{\circ}$ .

The phloroglucinol derivative was not isolated in a pure state.

The resorcinol and phloroglucinol derivatives give, with bromine, a precipitate which does not redissolve when excess of bromine is added and the liquid heated. With bromine, the catechol derivative gives a precipitate which dissolves in excess of bromine water. The pyrogallol derivative does not give a precipitate with bromine water.

These compounds resemble some of the natural tannins in many

ways, especially in their action towards bromine and towards iron salts.

When glyoxylic acid and paratoluidine act on one another, *paratoluidineacetoparatoluide*,  $C_7H_7 \cdot N \cdot CH \cdot CO \cdot NH \cdot C_7H_7$ , is formed together with small quantities of paratoluidineacetic acid and *paratoluyloparamethylmesatin*. The toluidine is a pale red, amorphous powder, soluble in benzene and alcohol, insoluble in dilute alkalis. The imesatin crystallises in scales melting at  $259^\circ$  and soluble in alcohol, sparingly so in benzene.

L. T. T.

**Triacetyl gallic acid.** By HUGO SCHIFF (*Bull. Soc. Chim.*, 1894, [3], 11, 770—771).—A question of priority with P. Sisley (this vol., i, 283) and A. Biétreix (*Abstr.*, 1894, i, 130).

J. N. W.

**Syntheses by means of Ethylic Phenylmalonate.** By WILHELM WISLICENUS and KARL GOLDSTEIN (*Ber.*, 1895, 28, 815—818; compare *Abstr.*, 1894, i, 376).—*Ethylic phenylmethylmalonate* may be prepared in the usual way, and boils at  $165$ — $166^\circ$  (16 mm. pressure). It is usually accompanied by a little ethylic phenylacetate, probably formed by the action of water in the presence of sodium ethoxide. *Phenylmethylmalonic acid* melts and loses carbonic anhydride at  $157^\circ$ , hydratropic acid,  $CHMePh \cdot COOH$ , being formed. *Ethylic phenylbenzylmalonate* boils at  $224^\circ$  (19 mm. pressure), and melts at  $48$ — $49^\circ$ . The free acid melts and decomposes at  $144^\circ$ . Only a very small amount of the acid is formed when the ethylic salt is hydrolysed, the greater part being converted into benzylphenylacetic acid.

A. H.

**Some Mercury Compounds of the Aromatic Series.** By AUGUST MICHAELIS (*Ber.*, 1895, 28, 588—593).—Compounds  $HgR_2$  ( $R$  = an aromatic residue) are obtained by heating the bromo-derivatives  $RBr$  in xylene solution at  $180^\circ$  with  $1\frac{1}{2}$ —3 per cent. sodium amalgam in amount containing twice the theoretical quantity of sodium. By heating them with alcoholic mercuric chloride compounds,  $Cl \cdot Hg \cdot R$  are obtained, and the corresponding bromo- and iodo-compounds may be similarly prepared. By dissolving them in a hot solution of a fatty acid,  $HX$ , and diluting the solution with water, compounds  $X \cdot Hg \cdot R$  are obtained. The temperatures given below are melting points.

1 : 3-*Mercuryditolyl*, colourless to pale yellow needles,  $102^\circ$ . 1 : 3-*Mercurytolyl bromide*, white needles,  $183$ — $184^\circ$ ; *iodide*, white, nacreous plates,  $161$ — $162^\circ$ ; *formate*, needles,  $106^\circ$ ; *acetate*, spherical aggregates of white needles,  $83$ — $84^\circ$ ; *propionate*, white needles,  $102^\circ$ . *Mercurydipseudocumyl*, white prisms,  $189^\circ$ . *Mercurypseudocumyl chloride*, needles,  $201^\circ$ ; *bromide*, white powder,  $211^\circ$ ; *iodide*, silky needles,  $196$ — $197^\circ$ . *Mercurydimesityl*, silvery needles,  $236^\circ$ . *Mercurymesityl chloride*, needles,  $200^\circ$ ; *bromide*,  $194^\circ$ ; *iodide*, needles,  $178^\circ$ . *Mercurycymyl chloride*,  $156^\circ$ ; *bromide*,  $163^\circ$ ; *iodide*,  $169^\circ$ ; all three crystallise in lustrous needles. *Mercurydiphenylenepheryl*,  $Hg(C_6H_4Ph)_2$ , lustrous scales,  $216^\circ$ ; the halogen compounds form white powders, and melt above  $325^\circ$ .

C. F. B.

### Oxidation of Derivatives obtained by the Action of Ortho- and of Para-toluenesulphonic Chloride on Amido-compounds.

By JULIUS TROEGER and PAUL W. UHLMANN (*J. pr. Chem.*, 1895, [2], 51, 435—448).—The authors make the interesting observation that well-formed crystals of paratoluenesulphonic chloride emit a bright light when pressed with a metal spatula or when shaken in the vessel containing them; this phenomenon is only exhibited by freshly formed crystals.

The oxidation of para- and ortho-toluenesulphonic anilide with potassium permanganate in a solution periodically neutralised with sulphuric acid, produced para- and ortho-toluenesulphonamide respectively.

The *condensation product*,  $C_6H_4Me \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot OH$ , obtained from paratoluenesulphonic chloride and paramidophenol, crystallises in white needles, and melts at  $143^\circ$ ; when oxidised by potassium permanganate in alkaline solution, it yields parasulphaminebenzoic acid, but if the oxidation occurs in neutral solution, paratoluenesulphonamide is produced. The *condensation product* of paratoluenesulphonic chloride with orthamidophenol crystallises in white needles, and melts at  $138$ — $139^\circ$ , whilst that with metamidophenol melts at  $157^\circ$ ; both yield paratoluenesulphonamide when oxidised in neutral solution.

The *condensation product* from paratoluenesulphonic chloride and phenylhydrazine,  $C_6H_4Me \cdot SO_2 \cdot N_2H_2Ph$ , melts at  $150$ — $151^\circ$ ; its oxidation has not been thoroughly investigated. A. G. B.

### Isomerism of the Diazosulphanilic acids and Diazo-ethers.

By ARTHUR HANTZSCH (*Ber.*, 1895, 28, 741—744).—Bamberger's observations on the transformation of paradiazosulphanilic acid into its isomeride by the action of soda (*Abstr.*, 1894, i, 295) cannot be confirmed. The acid condenses only in presence of alkali, whilst the iso-anti-salt does not form dyes even after remaining for weeks. Diazobenzenesulphonic acid behaves in a similar manner, and is little changed by 4 per cent. soda at ordinary temperatures even after several days' treatment. Iso-anti-nitrodiazobenzene cyanide combines directly with  $\beta$ -naphthol, but more slowly than the syn-derivative, and as the solution contains OH, not H, ions, isomeric change could not occur. The power of direct condensation shown by nitrodiazobenzene ether is therefore no proof that it does not belong to the iso-series (compare Bamberger, this vol., i, 134, and v. Pechmann, this vol., i, 215). In answer to Bamberger's other criticisms (this vol., i, 134 and 215), it is pointed out that the formation of normal potassium diazobenzene from various diazo-ethers is inconclusive, since the same compound is formed by the hydrolysis of nitrosoacetanilide. As Bamberger obtained ethers readily from the iso-anti-silver compounds, but not from the normal salts, the ethers should, according to his theory, belong to the same series. His results therefore confirm the author's view that the normal syn-ethers are incapable of existence. J. B. T.

**Hydrolysis of the Ethereal Salts of Sulphonic acids by Alcohols.** By J. H. KASTLE and PAUL MURRILL (*Amer. Chem. J.*, 1895, 17, 290—297).—Krafft and Roos (*Abstr.*, 1892, 1219; 1894, i, 91) have shown that the ethereal salts of sulphonic acids—in contradistinction to those of carboxylic acids—readily undergo hydrolysis when treated with alcohol, and can therefore be used for the preparation of ethers (alkyl oxides). The authors have studied the hydrolysis of ethylic benzenesulphonate, and ethylic parachlor-, parabrom-, and pariodo-benzenesulphonates in the presence of various alcohols. The last-named salt,  $C_6H_4I \cdot SO_3Et$ , is new, and was prepared by treating the corresponding sulphochloride with sodium ethoxide. It separates from ether in large, four-sided, transparent prisms, and melts at  $51^\circ$ .

Tables and curves showing how the amount of ethereal salt hydrolysed varies (1) with the amount of alcohol present, (2) with the kind of alcohol used, and (3) with the temperature, are given. The general conclusions arrived at are as follows:—(1) The ethereal salts of sulphonic acids are readily hydrolysed by alcohols. (2) The rate of hydrolysis increases with the temperature. (3) Of the alcohols tried (methylic, ethylic, normal- and iso-propylic alcohol); methylic alcohol is the most effective, the others seem to have practically the same effect. (4) The ethereal salts of halogen sulphonic acids are more readily hydrolysed than the corresponding salts of simple sulphonic acids; and the rate of hydrolysis appears to be independent of the nature of the halogen atom, as the ethereal salts of parachlor-, parabrom-, and pariodo-benzenesulphonic acids practically are hydrolysed to the same extent when treated with alcohol for a given time.

J. J. S.

**Action of Alkali Sulphites on Aromatic Diazo-compounds.** By HANS v. PECHMANN (*Ber.*, 1895, 28, 863—868).—Spiegel (*Abstr.*, 1885, 987) has shown that compounds containing the azo-group are capable of uniting with alkali hydrogen sulphites to form additive compounds; it is now shown that compounds which contain the diazo-group have the same property. Thus potassium sulphanilic-diazosulphonate,  $SO_3K \cdot C_6H_4 \cdot N \cdot N \cdot SO_3K$ , when treated with potassium sulphite, gives the salt of a trisulphonic acid,



This salt is very soluble in water, but can be precipitated with alcohol. It crystallises with  $3H_2O$ , and on heating with hydrochloric acid is hydrolysed into sulphuric acid and phenylhydrazineparasulphonic acid. This salt is characterised by its remarkable stability in the presence of Fehling's solution. When diazobenzene potassium sulphonate is heated for some time with a solution of potassium hydrogen sulphite, the main product is not a simple additive compound, but a salt of sulphanilic-hydrazo-sulphonic acid,



The formation of this salt is due to the removal of a sulphonic acid group from the side chain into the benzene nucleus, a phenomenon



similar to that observed by A. W. Hofmann and Martius in the case of the substituted aromatic amines.

The author thinks it probable that the first product formed on sulphonating an aromatic base is one in which the sulphonic group is in the side chain, and that this sulphonic group then replaces an atom of hydrogen in the benzene nucleus. J. J. S.

**Benzenesulphinic acid Derivatives of Diazobenzene.** By HANS V. PECHMANN (*Ber.*, 1895, **28**, 861—863).—The author considers that if the two isomeric series of benzenediazosulphonates described by Hantzsch (*Abstr.*, 1894, i, 455) are really stereoisomerides as Hantzsch asserts, then the probability is that the benzenediazosulphinic acids will also exist in two isomeric forms; but if the diazosulphonates are structurally isomeric, the isomerism depending on the tautomeric nature of the sulphinic acid group, as Bamberger (this vol., i, 25), E. Fischer (*Abstr.*, 1894, i, 597), and A. Claus (*Abstr.*, 1894, i, 597) believe, then the diazosulphinic acids will exist in one form only. From a study of the action of benzenesulphinic acid on diazobenzene and on paranitrodiazobenzene, under varying conditions, the author is led to the view that diazobenzene benzenesulphinate,  $\text{Ph}\cdot\text{N}_2\cdot\text{SO}_2\text{Ph}$ , and benzenesulphoparanitrodiazobenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SO}_2\text{Ph}$ , each exist in only one modification. The stereochemical theory of Hantzsch thus receives no support from the study of the sulphinic acids. J. J. S.

**A New Mode of Preparing Derivatives of Indole.** By EMIL FISCHER and HUGO HÜTZ (*Ber.*, 1895, **28**, 585—587).—When  $\alpha$ -benzoïnoxime,  $\text{NOH}\cdot\text{CPh}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_5$ , is dissolved in strong sulphuric acid, and the solution allowed to remain, it is converted almost quantitatively into 2'-phenylindoxyl,  $\text{CPh}\langle\begin{smallmatrix} \text{C}(\text{OH}) \\ \text{NH} \end{smallmatrix}\rangle\text{C}_6\text{H}_5$ ; zinc chloride at  $100^\circ$  effects the same transformation, but the yield is not so good. Neither  $\beta$ -benzoïnoxime nor deoxybenzoïnoxime ( $\alpha$ ) nor phenylacetoxime (? phenylacetaldoxime) undergo a similar transformation.

2'-Phenylindoxyl crystallises in small, lustrous, yellow needles, and melts at about  $175^\circ$  when quickly heated. It is reduced to 2'-phenylindole by zinc and acetic acid, or by hydriodic acid in acetic acid solution. C. F. B.

**Derivatives of Phenylindoxazen.** By PAUL COHN (*Monatsh.*, 1894, **15**, 645—664).—When phenylindoxazen (10 grams) is warmed for half an hour with 40 per cent. anhydrosulphuric acid (60 c.c.), phenylindoxazendisulphonic acid is formed, which yields the following derivatives:—A barium salt,  $\text{C}_{13}\text{H}_7\text{NO}_7\text{S}_2\text{Ba} + \text{H}_2\text{O}$ , which crystallises from hot water in white scales; a lead salt,  $\text{C}_{13}\text{H}_7\text{NO}_7\text{S}_2\text{Pb}$ , which is anhydrous; a sodium salt,  $\text{C}_{13}\text{H}_7\text{NO}(\text{SO}_3\text{Na})_2 + 2\text{H}_2\text{O}$ , which, on fusion with potash, yields a product melting at  $189^\circ$ , and containing 60.6 per cent. of carbon and 3.71 per cent. of hydrogen; a potassium salt,  $\text{C}_{13}\text{H}_7\text{NO}(\text{SO}_3\text{K})_2 + \text{H}_2\text{O}$ ; a silver salt,  $\text{C}_{13}\text{H}_7\text{NO}_7\text{Ag}_2$ ; and a sulphonamide, which melts at  $187$ — $188^\circ$ .

On bromination, phenylindoxazen yields a dibromo-derivative,

$C_{13}H_7NOBr_2$ , which crystallises in small, white needles, melts at  $148-149^\circ$ , and does not lose bromine when boiled in a reflux apparatus with sodium ethoxide for 4 hours.

On reduction of its alcoholic solution with sodium, phenylindoxazen is converted into *phenylorthocresolamine*,  $HO \cdot C_6H_4 \cdot CHPh \cdot NH_2$ , which melts at  $102-103^\circ$ , has a slight aromatic odour, dissolves readily in acids and alkalis, and yields the following salts ( $R = C_{13}H_{13}NO$ ):—*hydrochloride*,  $RHCl$ , which melts at  $194-196^\circ$ ; *platinochloride*,  $R_2H_2PtCl_6$ , which crystallises in orange-yellow needles; *hydriodide*,  $RHI$ , which crystallises in silky white needles softening at  $180^\circ$ ; *sulphate*,  $R_2H_2SO_4$ , which softens at  $180^\circ$ , and *nitrate*,  $RHNO_3 + H_2O$ , which melts at  $98^\circ$ . The *oxalate*, *picrate*, *tartrate*, and *dibenzoate* are also described. The last-named,  $C_{27}H_{21}NO_3$ , melts at  $176^\circ$ , and on boiling with alcoholic soda gives the *monobenzoyl derivative*,  $C_{20}H_{17}NO_2$ , which melts at  $208^\circ$ .

G. T. M.

**2 : 2'-Hydroxydiphenylcarboxylic Lactone (Diphenylmethylolid).** By CARL GRAEBE and P. SCHESTAKOW (*Annalen*, 1895, **284**, 306—324).—Diphenylmethylolid and xanthone are related in a similar manner to phenanthraquinone and anthraquinone respectively; the steps by which the former substance is obtained from phenanthraquinone include the preparation of the amide of fluorenonecarboxylic acid (Wegerhoff, *Abstr.*, 1888, 1201), orthamidofluorenone, and orthohydroxyfluorenone, the latter, on treatment with fused potash, giving rise to 2 : 2'-hydroxydiphenylcarboxylic acid, which is at once converted into the lactone.

*Orthamidofluorenone*,  $\begin{matrix} NH_2 \cdot C_6H_3 \\ | \\ C_6H_4 \end{matrix} > O$ , is obtained by the action of potassium hypobromite on the amide of fluorenonecarboxylic acid. It crystallises in long, slender, reddish-yellow needles, and melts at  $138^\circ$ ; it distils without undergoing decomposition. Fusion with caustic potash converts it into phenanthridone. The *hydrochloride* and *sulphate* are decomposed by water and alcohol; nitrous acid gives rise to a *diazo-derivative*, which yields hydroxyfluorenone on treatment with boiling water. During the preparation of orthamidofluorenone in the manner described, a varying amount of the *nitrile* of orthofluorenonecarboxylic acid is produced; it crystallises from alcohol in yellow needles, and melts at  $244^\circ$ .

*Orthohydroxyfluorenone*,  $\begin{matrix} HO \cdot C_6H_3 \\ | \\ C_6H_4 \end{matrix} > O$ , is prepared by adding sodium nitrite to the ice-cold solution of orthamidofluorenone in concentrated hydrochloric acid; it forms orange-red crystals, and melts at  $249^\circ$  (corr.), subliming and distilling without decomposition. It is readily soluble in alkalis, and, when warmed, in alkali carbonates. Treatment with fused potash converts it into a mixture of 2 : 2'- and 2 : 6-hydroxydiphenylcarboxylic acids.

2 : 2'-*Dihydroxydiphenylcarboxylic lactone*,  $\begin{matrix} C_6H_4 \cdot CO \\ | \\ C_6H_4 \cdot O \end{matrix}$ , is obtained by the action of fused potash on orthohydroxyfluorenone, 2 : 2'-hydroxydiphenylcarboxylic acid being the intermediate product; it is identical

with Richter's hydroxydiphenyleneketone (Abstr., 1884, 324), prepared by the action of phosphorus oxychloride on sodium or methylic salicylate, and subsequently by Griess by heating phenol with the sulphate of orthodiazobenzoic acid on the water bath (Abstr., 1888, 588), this method of preparation also giving rise to phenylsalicylic acid and 2 : 4'-hydroxydiphenylcarboxylic acid. It crystallises from alcohol in needles, and melts at  $92.5^{\circ}$  (corr.); on adding silver nitrate to the neutral solution of the potassium salt, silver hydroxydiphenylcarboxylate is formed. It is readily soluble in alkalis, whilst alkali carbonates dissolve it only when warmed, and a current of carbonic anhydride reprecipitates the lactone. It is indifferent towards phenylhydrazine and reducing agents, and when distilled with zinc dust yields diphenyl; distillation from lime gives rise to diphenylene oxide and benzophenone, whilst the calcium salt of 2 : 2'-hydroxydiphenylcarboxylic acid gives rise to 2-hydroxydiphenyl when submitted to dry distillation.

2 : 6-Hydroxydiphenylcarboxylic acid is one of the products of the action of fused potash on orthohydroxyfluorenone. It crystallises from water with  $1\text{H}_2\text{O}$ , which is lost at  $100^{\circ}$ ; the anhydrous salt melts at  $154^{\circ}$  (corr.). Treated with excess of lime water, it forms a *dicalcium* salt, which becomes converted into the *monocalcium* salt under the influence of carbonic anhydride. The lactone is not formed on treating the acid with acetic chloride, and the action of cold, concentrated, sulphuric acid converts it into orthohydroxyfluorenone. The *methylic* salt melts at  $84\text{--}85^{\circ}$ , and distils without undergoing decomposition; the *ethylic* salt crystallises from alcohol in plates, and melts at  $111^{\circ}$ . The amide is obtained by heating the ammonium salt in sealed tubes for six hours at  $250\text{--}260^{\circ}$ ; it crystallises from alcohol in needles, and melts at  $262\text{--}263^{\circ}$ .

4' : 2-Hydroxydiphenylcarboxylic acid is formed during the preparation of diphenylmethylid from phenol and orthodiazobenzoic acid: it melts at  $206.5^{\circ}$ , and its properties agree with those of the substance described by Griess (*loc. cit.*). M. O. F.

**Action of Ethylic Oxalate on Dibenzyl Ketone.** By LUDWIG CLAISEN and THOMAS EWAN (*Annalen*, 1895, 284, 245—299; compare Abstr., 1888, 676, and 1891, 425).—Continuing the investigation of the behaviour of ethylic oxalate towards ketones (*loc. cit.*), the authors have included diethyl ketone and dibenzyl ketone in their experiments.

Diethyl ketone, when mixed with ethylic oxalate (1 mol.) and treated with ice-cold alcoholic sodium ethoxide (1 mol.), gives rise to a compound,  $\text{C}_7\text{H}_8\text{O}_3$ , with elimination of 2 mols. of ethylic alcohol. The same substance is produced when methylic oxalate and sodium methoxide are employed; it melts at  $142\text{--}143^{\circ}$ , and has strongly acid properties. An intense, dark-green coloration is developed in the alcoholic solution by ferric chloride.

Oxalyldibenzyl ketone,  $\text{C}_{17}\text{H}_{12}\text{O}_3$ , is obtained by adding a mixture of dibenzyl ketone (1 mol.) and ethylic oxalate (1 mol.) to an ice-cold solution of sodium (2 mols.) in absolute alcohol; the liquid, which at first becomes brown and finally bluish-violet, is cooled for a few

hours, and then allowed to remain at the ordinary temperature for two days. The same compound is produced when methylic oxalate and methylic alcohol are used. It crystallises in short, sulphur-yellow prisms, and melts at  $192\text{--}193^\circ$ ; at  $194\text{--}196^\circ$  it resolidifies, and melts finally at  $240^\circ$ . The alcoholic solution gives a yellowish-brown or brownish-green coloration with ferric chloride, according to the quantity of reagent employed, whilst copper acetate also colours the liquid yellowish-brown; if the solution is dilute, the latter reagent produces a yellowish coloration, which becomes green, a yellow copper salt being precipitated. When heated with oxalyldibenzyl ketone dissolved in sodium carbonate, Fehling's solution is at once reduced; on adding fuming nitric acid to the solution in glacial acetic acid, and pouring the liquid into water, a yellow precipitate is formed, which dissolves in alkalis with a blue colour. Oxalyldibenzyl ketone has strongly acid properties, and is not completely precipitated from solutions of its salts by acetic acid, whilst an aqueous solution of potassium acetate dissolves it when heated on the water bath; the *sodium* and *potassium* salts are yellow, and the *silver* salt is not decomposed by light. On adding one drop of caustic soda to a solution of the sodium salt, a yellow coloration is produced, becoming brownish-violet, whilst the liquid acquires an intense, bluish-violet colour on further addition of alkali. When oxalyldibenzyl ketone is heated with aqueous potash for half an hour, it is decomposed into dibenzyl ketone and oxalic acid. Ammonia converts it into a *compound*,  $\text{C}_{17}\text{H}_{11}\text{O}_2\cdot\text{NH}_3$ , which separates from glacial acetic acid in compact, lustrous crystals, and melts at  $151\text{--}152^\circ$ ; it dissolves in alkalis and alkali carbonates, gives a brownish-green coloration with ferric chloride, and yields an *isomeride* when heated at  $200^\circ$ . This substance crystallises in lustrous, yellow leaflets, and melts at  $226\text{--}227^\circ$ ; the solution in sodium carbonate is yellow, and does not yield ammonia when boiled, differing in this respect from the first modification. The *anilide*,  $\text{C}_{17}\text{H}_{11}\text{O}_2\cdot\text{NHPh}$ , crystallises from alcohol in short, yellow needles, and melts at  $175\text{--}176^\circ$ ; it is insoluble in aqueous alkalis, which dissolve it, however, if alcohol is previously added, the first few drops producing a violet coloration. Acetic acid precipitates the anilide and the two isomeric ammonium derivatives from the solutions in alkali. Orthotolylenediamine gives rise to a *compound*,  $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}$ , which crystallises in orange-coloured plates, and melts at  $290\text{--}291^\circ$ ; the alcoholic solution exhibits fluorescence, yellow in transmitted, green by reflected light. The *phenylhydrazone*,  $\text{C}_{17}\text{H}_{12}\text{O}_2\cdot\text{N}\cdot\text{NHPh}$ , melts at  $181\text{--}182^\circ$ , and the solution in concentrated sulphuric acid is deep red, becoming blue on the addition of ferric chloride; it has acid properties, and is precipitated from the solutions in alkalis by acetic acid. Hydroxylamine gives rise to a *derivative*,  $\text{C}_{17}\text{H}_{13}\text{NO}_3$ , which in behaviour more closely resembles a carboxylic acid than an oxime; it melts and decomposes at  $183\text{--}184^\circ$ , and is precipitated from alkaline solutions on the addition of mineral acids only.

The *acetyl* derivative of oxalyldibenzyl ketone crystallises in yellow needles, and melts at  $103\text{--}104^\circ$ ; it has acid properties, and the *potassium* salt, which is deep violet, yields oxalyldibenzyl ketone when the aqueous solution is treated with hydrochloric acid.

The *methylic* salt,  $C_{17}H_{11}O_3Me$ , is obtained by acting on the dry silver salt of oxalyldibenzyl ketone with methylic iodide; it crystallises in short, yellow needles, and melts at  $94-95^\circ$ . Although scarcely soluble in cold, aqueous potassium carbonate, it dissolves readily when heated, with production of an intense, violet coloration. It is hydrolysed by hot aqueous alkalis.

The isomeric *methylic* derivative,  $C_{17}H_{11}O_3Me$ , is obtained by adding methylic iodide to an alcoholic solution of the disodium salt of oxalyldibenzyl ketone; it crystallises in sulphur-yellow leaflets, and melts at  $167^\circ$ . It dissolves in aqueous potassium carbonate, and on adding silver nitrate to the neutral solution the *silver* salt is precipitated. The action of hot aqueous alkali gives rise to oxalic acid and *methyldibenzyl ketone*,  $CHPhMe \cdot CO \cdot CH_2Ph$ , an oil which boils at  $320-326^\circ$ , and yields a *phenylhydrazone*, which melts at  $92-93^\circ$ . The *acetyl* derivative,  $C_{17}H_{10}O_3MeAc$ , crystallises in short, yellow prisms, melts at  $111-112^\circ$ , and dissolves in alkali carbonates.

The *dimethyl* derivative,  $C_{17}H_{10}O_3Me_2$ , is obtained by the action of methylic iodide on the silver salt of the foregoing compound. It crystallises in lustrous, yellow cubes, and melts at  $79^\circ$ . Although insoluble in cold alkalis and alkali carbonates, it yields the monomethyl derivative when boiled for several hours with aqueous potash.

Oxalyldibenzyl ketone is oxidised by potassium permanganate, with formation of benzoic and oxalic acids, and a *compound*,  $C_{17}H_{10}O_3$  or  $C_{34}H_{22}O_6$ . The latter, however, is more conveniently obtained by the action of mercuric oxide suspended in the hot, aqueous solution; it crystallises from ethylenic bromide in pale yellow plates, becomes brown at  $225^\circ$ , and melts at  $237-239^\circ$ , undergoing decomposition; the substance retains the solvent from which it is crystallised. Ferric chloride develops in the alcoholic solution a dark, brownish-green coloration, whilst copper acetate gives rise to a yellow precipitate; Fehling's solution is not reduced when boiled with the substance. It dissolves in alkalis, alkali carbonates, and, on heating, in alkali acetates, and the dilute alcoholic solution is strongly acid. The *sodium* salt contains  $3H_2O$ ; the *silver* salt is yellow.

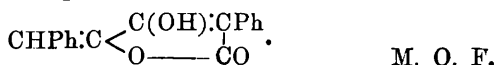
When heated at  $225-230^\circ$ , oxalyldibenzyl ketone is converted into an isomeride, which crystallises in silvery, greyish-yellow leaflets, and melts at  $248-249^\circ$ , undergoing decomposition. *Iso-oxalyldibenzyl ketone* has strongly acid properties; the *potassium* and *sodium* salts contain  $4H_2O$ , and the solution of the latter does not become violet on adding excess of alkali. The *barium* salt contains  $8H_2O$ ; the *silver* salt is not readily decomposed by light, and the *methylic* salt appears to be an oil. The *acetyl* derivative crystallises from methylic alcohol in pale yellow needles, and melts at  $137-139^\circ$ .

When oxidised with potassium permanganate, *iso-oxalyldibenzyl ketone* gives rise to benzaldehyde, and oxalic, benzoic, and benzoylformic acids. On reduction with sodium amalgam, a *dihydro*-derivative,  $C_{17}H_{14}O_3$ , is produced; it crystallises from glacial acetic acid in colourless leaflets, and melts at  $220-221^\circ$ .

The behaviour of *iso-oxalyldibenzyl ketone* towards hot aqueous alkalis has an important bearing on the question of its constitution. Whilst potash decomposes it into dibenzylglycollic acid (m. p.

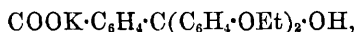
157—158°) and carbonic anhydride, treatment with aqueous barium hydroxide gives rise to dibenzyl ketone, phenylacetic, phenylpyruvic, and dibenzylglycollic acids, together with a dibasic acid of the formula  $C_{17}H_{16}O_5$ . A close comparison of the chemical characteristics of iso-oxalyldibenzyl ketone and dibenzylloxalylcarboxylic acid lactone (Volhard, this vol., i, 100), supplemented by an examination of their toxic properties, renders it probable that these two substances differ only tautomerically. In order to emphasise the relation of iso-oxalyldibenzyl ketone to derivatives of pulvic acid, the authors propose to term it *pulvinone*.

Consideration of the properties of oxalyldibenzyl ketone leads to the formula  $CHPh \begin{smallmatrix} \diagup CO \cdot CPh \\ \diagdown CO \cdot C \cdot OH \end{smallmatrix}$  as expressing its constitution, whilst the isomeric pulvinone is represented by the formula



**Phenolphthaleïn Derivatives.** By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1895, 120, 296—299).—The action of phthalic chloride on phenylic ethylic ether in presence of aluminium chloride yields the *diethylphenolphthaleïn*,  $\begin{smallmatrix} C_6H_4 \\ | \\ CO \cdot O \end{smallmatrix} > C(C_6H_4 \cdot OEt)_2$ , a white, crystalline compound, very soluble in benzene, much less soluble in alcohol or ether. It dissolves in concentrated sulphuric acid, forming a red solution, from which it is precipitated without alteration, on dilution.

When boiled with ethylic iodide in presence of sodium ethoxide, phenolphthaleïn yields a diethyl derivative identical with the preceding compound, and not a diethyl derivative with a quinonoid constitution. If either of the products is heated with alcoholic potash, it yields slender, white needles of the salt,



which gradually dissociates in presence of water, regenerating diethylphenolphthaleïn, thus resembling the dibenzyl derivative. Sodium amalgam or zinc powder in presence of aqueous potash readily and quantitatively converts the diethyl derivative, by whichever method prepared, into *diethoxytriphenylmethaneorthocarboxylic acid*,  $COOH \cdot C_6H_4 \cdot CH(C_6H_4 \cdot OEt)_2$ ; this forms colourless crystals melting at 135°, and somewhat soluble in the ordinary solvents, and in solutions of alkali hydroxides and carbonates; sulphuric acid in the cold converts it into a well-crystallised phthalidin.

Although there is no evidence of a quinonoid grouping in diethylphenolphthaleïn, the author does not consider that it necessarily follows that phenolphthaleïn has not a quinonoid function in alkaline solution.

C. H. B.

**Formation of Diphthalyl.** By GUIDO GOLDSCHMIEDT (*Monatsh.*, 1895, 16, 13—16).—When phthalide and ethylic- $\psi$ -opiate are heated together in molecular proportion at 280—290°, diphthalyl, in yield of

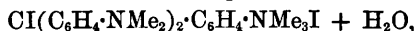
from 4 to 5 per cent., is obtained. When dissolved in concentrated sulphuric acid, it forms a pale yellow solution having a strong blue fluorescence, and on the addition of sulphuric acid containing a trace of nitric acid to this solution, an evanescent emerald-green coloration is observed. These colour reactions afford a convenient method of characterising diphthalyl (compare Gräbe and Guye, *Abstr.*, 1886, 882).

G. T. M.

### Hexamethyltriamidotriphenylmethane Derivatives.

By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1895, **120**, 192—194, 264—266, and 331—333).—When sodium hydroxide is added to a boiling solution of hexamethyltriamidotriphenylmethane chloride in methylic, ethylic, or amylic alcohol, the product is not the carbinol corresponding with the chloride, but an ether of the type  $\text{OR}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ . When  $\text{R} = \text{Me}$  or  $\text{Et}$  the product is crystalline, but the amylic derivative is viscous. When treated with methylic iodide in the cold in presence of water or alcohol, these derivatives, as well as the corresponding carbinol and hydride, all combine with three molecules of methylic iodide, yielding crystalline, white or sulphur-yellow products, soluble in water and in alcohol, but insoluble in other organic solvents. They decompose below  $100^\circ$  with loss of methylic iodide, and become blue. When heated with alcoholic soda, the original triamine is obtained together with the intermediate products described below. Silver oxide removes the iodine and forms powerful bases which combine with hydrogen iodide and behave like the octomethyleucaniline of Hofmann and Girard. The solubilities of the five compounds at  $16\text{--}20^\circ$  show considerable differences; the carbinol is more soluble than the hydride, and the solubility of the ethereal salts increases with the molecular weight of the introduced alkyl radicle.

The action of methylic iodide on hexamethyltriamidotriphenylmethane gives rise to intermediate products which become green in contact with hot acetic acid, but only one of these could be isolated. The methoxide,  $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ , is mixed with water and methylic iodide, and allowed to remain at the ordinary temperature for several days, until, in contact with dilute acetic acid, a green colour is produced instead of a violet. The product is then mixed with water, the excess of methylic iodide removed by distillation, and the liquid filtered. The triiodo-compound is in the solution; the intermediate product remains on the filter and is purified by crystallisation from methylic alcohol. The moniodotrimethylammoniumtetramethyldiamidotriphenylmethane methoxide,  $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ , thus obtained is white and crystalline; when dissolved in dilute acetic acid and mixed with a small quantity of an aqueous solution of potassium iodide, it yields a lustrous crystalline mass of the compound



which is the lower homologue of "iodine-green" and like the latter is unstable. When heated, it loses water and methylic iodide, and yields hexamethyltriamidotriphenylmethane iodide, but if heated in a current of methylic iodide vapour at  $100^\circ$  it loses water only.

The moniodo-ammoniums corresponding with the other four triamines are formed when the triiodoammoniums are treated with aqueous

soda in the case of the ethylic and amylic compounds, or alcoholic soda in the case of the lower terms; after boiling for some hours and then adding acetic acid a green product is obtained. In the case of the derivative of the hydride, lead peroxide must be added with the acetic acid, and the iodide  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$  is formed.

The compounds described above include three that are coloured and eleven that are colourless, but six of the latter can be converted into coloured compounds by double decomposition. They are as follows—

*Coloured compounds.*— $\text{CCl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ , and the corresponding iodide, and  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ .

*Colourless compounds yielding coloured products.*— $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ ,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ , and the corresponding methylic, ethylic, and amylic ethers, and  $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$ .

*Colourless compounds yielding colourless products.*— $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3$ ,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3$ , and the corresponding methylic, ethylic, and amylic ethers.

The coloured compounds have a negative element or an acid radicle united with the carbon of the methane nucleus, the three other valencies of this carbon being satisfied by the amidophenyl group in which the nitrogen is trivalent, except in the third compound where one of the nitrogens is quinquevalent. This characteristic is shared by the compounds in the second group, but in these the radicle saturating the fourth valency of the methane carbon shows considerable chemical activity, and when positive can be displaced by a negative radicle and *vice versa*, a negative radicle producing a coloured compound and a positive radicle a colourless one.

In the third group of compounds, the nitrogen of the amidophenyl groups is in all cases quinquevalent, and the univalent groups H, OH, OMe, &c., are no longer replaceable by negative radicles. The complete saturation of the nitrogen therefore involves the immobility of the positive radicle attached to the methane carbon, and this gives the whole molecule a much higher stability.

In the carbinol  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3$  the hydroxyl group cannot be displaced by an acid radicle, but can be displaced by an alkyl group, and in this respect it resembles triphenylcarbinol, the saturation of the nitrogen imparting to the group  $\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$  functions similar to those of the group  $\text{C}_6\text{H}_5$ .

The alcoholic function of triphenylcarbinol resembles that of acids, and the corresponding chloride is decomposed by cold water; the alcoholic function of  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ , on the other hand, is of the same order as that of metallic hydroxides, since it reacts with acids, and the amidocarbinols in general displace ammonia from its salts. The intermediate condition is represented by the diamidocarbinols.

C. H. B.

**Triphenylmethane Colouring Matters.** By ALBIN HALLER and PAUL TH. MULLER (*Compt. rend.*, 1895, 120, 410—413).—Ebullioscopic determinations lead to the conclusion that the chlorides of the colouring matters of the amidotriphenylmethane group are not dissociated in water, whereas ammonium chloride, aniline hydrochloride, and nitrosodimethylaniline hydrochloride show considerable dissociation.



This result supports Rosenstiehl's view as to the constitution of the rosaniline and other triphenylmethane colouring matters.

C. H. B.

**Preparation of  $\alpha$ -Naphtholcarbothionylic acid.** By RICHARD PIRRAM and CARL GLÜCKSMANN (*Monatsh.*, 1894, **15**, 605—612; compare Abstr., 1893, i, 75).—On heating  $\alpha$ -naphthol (20 grams) with potassium thiocarbonate (30 grams) in sealed tubes at 125—130°,  $\alpha$ -naphtholcarbothionylic acid is obtained in yield of about 10 per cent. It is a dark yellow powder, which gives a red coloration with alkaline solutions, is only sparingly soluble in alcohol, ether, water and benzene, and melts with decomposition at 110°. A better yield (70 per cent.) of the acid is obtained on heating together  $\alpha$ -naphthol, potassium xanthate, and alcohol, at 100°. The potassium derivative of  $\alpha$ -naphthol and carbon bisulphide, when heated in sealed tubes at 100°, also combine with formation of the potassium salt of  $\alpha$ -naphtholcarbothionylic acid.

G. T. M.

**Synthesis of Anthracene.** By MAURICE DELACRE (*Compt. rend.*, 1895, **120**, 155—157).—The action of ethylic trichloracetate on benzene in presence of aluminium chloride yields a product which crystallises readily in bulky needles, melting at 219°. When more strongly heated, it yields carbonic anhydride and a hydrocarbon which melts at 115° and boils at about 300°. The exact nature of the first product and of the hydrocarbon derived from it were not ascertained.

The action of phenylic trichloracetate on benzene in presence of aluminium chloride, yields an ethereal salt which is difficult to isolate but which when distilled splits up into carbonic anhydride and anthracene, about 9 grams of the latter being obtained from 20 grams of phenylic trichloracetate.

C. H. B.

**Orientation in the Terpene Series.** By ADOLF BAEYER (*Ber.*, 1895, **28**, 639—652, and 652—654; compare Abstr., 1894, i, 535, and this vol., i, 152).—*d*-Carone, obtained from caraway oil, has  $[\alpha]_D = +173.8^\circ$ ; the sp. gr. is 0.9567. *l*-Carone, derived from balm-mint (*Mentha crispa*) oil, has  $[\alpha]_D = -169.5^\circ$ . Each modification forms a liquid oxime, and on mixing the two, the oxime of *i*-carone separates; it crystallises in long prisms, and melts at 77—79°. The semicarbazide compound of the inactive modification melts at 178°.

*d*-Bisnitrosocarone,  $(C_{10}H_{15}O)_2N_2O_2$ , is obtained by cautiously adding acetic chloride to a well-cooled mixture of *d*-carone and amyl nitrite; it crystallises in small, colourless plates, and decomposes and evolves gas at 112—118°, a green coloration being developed. This substance closely resembles bisnitrosylbenzyl (Behrend and Königs, Abstr., 1890, 1122), differing from it, however, in its behaviour on treatment with hydrolysing agents; this is probably due to its tertiary character, whilst bisnitrosylbenzyl must be regarded as a primary bisnitroso-derivative. *i*-Bisnitrosocarone crystallises in rhombic plates; it melts and decomposes at 145°.

*Caronedinitrosylic acid*,  $C_{10}H_{15}O \cdot N_2O_2 \cdot H$ , is formed when bisnitrosocarone is treated with an ice-cold solution of hydrogen chloride in absolute alcohol. It melts and decomposes at  $80-90^\circ$ , and in many respects resembles nitroso- $\beta$ -benzylhydroxylamine, obtained by the action of nitrous acid on  $\beta$ -benzylhydroxylamine (Behrend and Königs, Abstr., 1891, 1034).

The *dinitrin*,  $C_{20}H_{32}N_2O_2$ , obtained by reducing dinitrosocarone in alcoholic solution with sodium amalgam, melts at  $120-130^\circ$ ; it undergoes decomposition spontaneously at ordinary temperatures, and also on treatment with cold mineral acids, in which it is very readily soluble. On reducing bisnitrosocarone with sodium amalgam, a certain quantity of *d*-carone is regenerated. The *dinitrosone*,  $C_{20}H_{32}N_2O_4$ , is formed on adding sodium hypochlorite to a solution of caronedinitrosylic acid in sodium carbonate.

Nitrosomenthone, nitrosodihydroeucarvone, and *nitrosocarveol*, which melts and decomposes at  $133^\circ$ , are bisnitroso-derivatives. Nitrosopinene, on the other hand, is an isonitroso-derivative, forming sodium and methylic salts, and yielding carvacrol when boiled with dilute hydrochloric acid for half an hour. In order to distinguish between carvacrol and thymol, a very dilute, alkaline solution of the phenol is treated with sodium nitrite and acidified; after some hours yellow needles are deposited, and on adding acetic acid to the solution of these crystals in ammonia, a solid, amorphous precipitate of the nitroso-derivative is formed if thymol is present, whilst carvacrol gives rise to oily drops which soon become crystalline. The formation of carvacrol when nitrosopinene is treated with boiling hydrochloric acid is not in accordance with Bredt's expression for the constitution of pinene, which demands the production of thymol under these conditions.

It is found that pinene and limonene nitrosochlorides are bisnitroso-derivatives belonging to the class of secondary compounds.

The *semicarbazide compound* of pulegone crystallises from alcohol and melts at  $172^\circ$ ; on treating it with boiling dilute acids, pulegone is regenerated.

*Pulegone hydrochloride* is obtained on adding pulegone to a cooled solution of hydrogen chloride in glacial acetic acid, the liquid being afterwards poured on to ice; it melts at  $24-25^\circ$  (compare Beckmann and Pleissner, Abstr., 1891, 936). The hydrochloride yields pulegone when treated with a solution of potash in methylic alcohol; it is more stable than the hydrobromide, from which pulegone is regenerated on treatment with silver acetate and acetic acid.

*Nitrosopulegone*,  $C_{10}H_{16}O \cdot NO$ , is obtained in long, slender needles; ammonia dissolves it, giving rise to an oxime. Nitrosopulegone is probably a secondary bisnitroso-derivative. M. O. F.

**Fenchone.** By OTTO WALLACH (*Annalen*, 1895, 284, 324—345; compare Abstr., 1893, i, 105 and 596).—A direct comparison has been made of metacymene obtained by the action of phosphoric anhydride on fenchone (*loc. cit.*) with metacymene isolated by Kelbe from resin oil, and it is found that the hydrocarbons are identical.

*Tetrahydrofenchene*,  $C_{10}H_{20}$ , is formed when fenchylic alcohol is

heated with phosphorus and hydriodic acid for 15 hours at 210—215°; it is a colourless oil which boils at 160—165°. The sp. gr. = 0.7945 at 22°, and the refractive power is  $[n]_D = 1.4370$ . The hydrocarbon is also obtained by reducing fenchone and fenchylamine under the conditions described; it is not identical, however, with the hydrocarbon formed on reducing fencholenic acid (Abstr., 1892, 1237), but in physical properties it closely resembles the tetrahydropinene obtained from pinene hydrochloride (Abstr., 1892, 998), although the two compounds are not identical. It resists the action of potassium permanganate and of fuming nitric acid in the cold; the bromide crystallises from ethylic acetate and melts at 200°.

*Fenchocarboxylic acid*,  $C_{11}H_{16}O_3$  or  $C_{11}H_{18}O_3$ , is formed on passing a current of carbonic anhydride through a solution of fenchone in ether to which sodium has been added; it has not been obtained free from acetic acid and fenchylic alcohol, and in this condition melts at 77—78°. The lead salt is amorphous. When submitted to dry distillation, the acid decomposes into carbonic anhydride and an unsaturated acid,  $C_{11}H_{16}O_2$ , which crystallises from alcohol in lustrous leaflets, and from ether in prisms, melting at 173—174°. It sublimes without undergoing change, is volatile in an atmosphere of steam, and is lævorotatory. The silver salt is unstable, and dissolves in alcohol and ether.

During the preparation of fenchocarboxylic acid, fenchylic alcohol is obtained in considerable quantity; it melts at 45° (compare Abstr., 1891, 1086). When added to a solution of phosphorus and iodine in carbon bisulphide, it yields a fenchylic phosphite which crystallises in needles and melts above 300°; if chlorine is employed, fenchylic chloride is formed, together with an isomeride which melts at 195—196°, and has an odour of camphor. The acid of the formula  $C_{10}H_{16}O_3$ , obtained by oxidising fenchone (*loc. cit.*), melts at 152°.

The substance hitherto described as  $\alpha$ -isofenchonoxime, melting at 113—114°, is, without doubt, *fencholenamide*; it yields fenchonitrile when treated with phosphoric anhydride, and is identical with the product obtained by heating ammonium fencholenate in sealed tubes at 205—210°. It is probable that  $\beta$ -isofenchonoxime is a lactam; it has basic properties, and is formed when fencholenamide is treated with dilute mineral acids.

When fencholenamide is reduced in alcoholic solution with sodium, fencholenic acid and fencholenamine are formed, together with *isofencholenic alcohol*,  $C_{10}H_{18}O$ , which boils at 218°, and is an unsaturated alcohol; its solution in glacial acetic acid becomes deep red on addition of concentrated sulphuric acid. The sp. gr. = 0.927 at 20°, and the refractive power is  $[n]_D = 1.476$ , or  $M = 47.04$ , the calculated value being  $M = 47.15$ .

*Fenchenole*,  $C_{10}H_{18}O$ , is obtained by heating isofencholenic alcohol with dilute sulphuric acid for eight hours in a reflux apparatus; it is isomeric with cineole, which it closely resembles, although it boils at 183—184°. The sp. gr. = 0.925 at 20°, and the refractive power  $[n]_D = 1.46108$ , or  $M = 45.69$ , the calculated value for a saturated oxide being  $M = 45.61$ . The formation of fenchenole affords an interesting parallel with the conversion into oxides of the alcohols

obtained from methyl hexylene ketone and methyl heptylene ketone (Abstr., 1893, i, 597).

The author discusses the behaviour of fenchone and its derivatives, and expresses its constitution by the formula

$$\begin{array}{c} \text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH} - \text{CO} \end{array} > \text{CMe}_2.$$

M. O. F.

**Occurrence of Citronellal in Citron Oil.** By OSCAR G. DOEBNER (*Arch. Pharm.*, 1894, **232**, 688—691).—The author has obtained the aldehyde citronellal,  $\text{C}_{10}\text{H}_{18}\text{O}$ , from citron oil as well as the related compound citral,  $\text{C}_{10}\text{H}_{16}\text{O}$ . These were separated as substituted cinchonic acids,  $\text{C}_9\text{H}_{17} \cdot \text{C}_{14}\text{H}_8\text{NO}_2$  and  $\text{C}_9\text{H}_{15} \cdot \text{C}_{14}\text{H}_8\text{NO}_2$ , by digesting the oil with pyruvic acid and  $\beta$ -naphthylamine. The citronellal acid forms crystals which are more easily soluble than those of the citral acid.

L. T. T.

**Action of Nitrous acid on Amidocamphor.** By ANGELO ANGELI (*Gazzetta*, 1894, **24**, ii, 317—325; compare this vol., i, 61).—Azocamphanone yields a *hydrazone* which crystallises in lustrous yellow scales melting at  $216^\circ$ , and when distilled with dilute sulphuric acid gives hydrazine sulphate and “camphadione,”  $\text{C}_8\text{H}_{14} < \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array}$ .

Camphenoneoxime in ethereal solution is converted by phosphorus pentachloride into a colourless, crystalline substance melting at  $87^\circ$ ; this is still under examination.

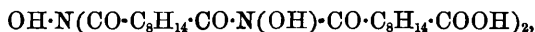
W. J. P.

**Bromo-Derivatives of the Camphor Series.** By ANGELO ANGELI and E. RIMINI (*Ber.*, 1895, **28**, 819—820).—Camphenone (this vol., i, 61) behaves as an unsaturated compound, decolorises permanganate solution, and is reduced to camphor by nascent hydrogen. It combines with hydrogen bromide to form a substance which melts at  $114^\circ$ , and is isomeric with bromocamphor. Camphenone also combines with bromine to form an oily product which, when treated with alcoholic potash, yields *monobromocamphenone*,  $\text{C}_{10}\text{H}_{13}\text{BrO}$ ; this crystallises well, and melts at  $70^\circ$ .

Monoketazocamphoquinone,  $\text{C}_{10}\text{H}_{14}\text{N}_2$ , also reacts with bromine, nitrogen being eliminated and an oily product formed.

A. H.

**Action of Hydroxylamine on Camphoric Anhydride.** By GIORGIO ERRERA (*Gazzetta*, 1894, **24**, ii, 336—348).—Sodium ethoxide dissolved in alcohol reacts readily with a boiling alcoholic solution of camphoric anhydride and hydroxylamine hydrochloride yielding a salt,  $\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}_{10}\text{Na}_2$ , which crystallises in needles on concentrating the solution, and is readily soluble in water; the corresponding lead compound,  $\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_{10}\text{Pb}_2$ , is a white powder insoluble in water. The corresponding acid, which probably has the constitution



cannot be prepared in the free state as its lead salt is decomposed by hydrogen sulphide into camphoric acid and *camphorylhydroxylamine*,

$C_8H_{14}<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>N\cdot OH(?)$ . The latter crystallises in lustrous, colourless, orthorhombic needles, melting at  $225-226^\circ$ ;

$$a : b : c = 1.0472 : 1 : 0.5596.$$

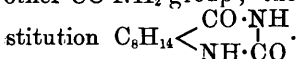
Its *sodium* derivative,  $C_{10}H_{14}NO_3Na$ , crystallises in colourless needles. The hydroxylamine is readily hydrolysed, yielding the corresponding *hydroxamic acid*,  $C_8H_{14}<\begin{smallmatrix} CO\cdot NH\cdot OH \\ COOH \end{smallmatrix}>$ , which could not be isolated.

The *copper* salt,  $C_8H_{14}<\begin{smallmatrix} CO\cdot NHO \\ COO \end{smallmatrix}>Cu, 2H_2O$ , is a green powder, soluble in water; on heating its aqueous solution, an insoluble *monohydrate*,  $C_{10}H_{15}NO_4Cu, H_2O$ , is deposited.

W. J. P.

### Action of Potassium Hypobromite on Camphoric Amide.

By GIORGIO ERRERA (*Gazzetta*, 1894, **24**, ii, 348—350).—The author employs a slightly modified form of Winzer's method (*Abstr.*, 1890, 1150) for preparing camphoric amide from ethylic camphorylmalonate. On allowing bromine to act on the amide, heat is developed, but no hydrogen bromide is evolved; and on pouring the mixture into potash, a white, crystalline *substance*,  $C_{10}H_{16}N_2O_2$ , melting at about  $235^\circ$ , separates; it is soluble in bases, alcohol, or water. Its formation is probably due to the conversion of one  $CO\cdot NH_2$  group of the amide into an isonitrile group, which then condenses with the other  $CO\cdot NH_2$  group; the new substance would thus have the constitution



W. J. P.

**Derivatives of Campholic Acid.** By GUERBET (*Bull. Soc. Chim.*, 1894, [3], **11**, 610—618).—*Campholic anhydride*,  $(C_{10}H_{17}O)_2O$  (molecular weight by cryoscopic method), is obtained by heating campholic acid with acetic anhydride or chloride, or by the action of campholic chloride on silver campholate. Like its derivatives, it is insoluble in water, but soluble in alcohol, ether, &c., separating from these solvents in large, colourless crystals, or slender needles; it melts at  $56^\circ$ , and boils at  $209-210^\circ$  (20 mm.). Campholic anhydride is slowly hydrolysed to the acid by aqueous or alcoholic potash, and is converted by alcohol into the ethylic salt, and by ammonia into the amide described by Errera (*Abstr.*, 1893, i, 108). The *amidide*, from the anhydride and aniline at  $100^\circ$ , crystallises in long needles, and melts at  $91^\circ$ ; it is easily hydrolysed by acids at  $150^\circ$ , but with difficulty by alkalis. The *phenylhydrazide*, prepared by boiling the anhydride with phenylhydrazine, forms nacreous crystals, and melts at  $171^\circ$ . In making campholic chloride from the acid and phosphorus pentachloride, the materials must be perfectly dry, as in presence of phosphoric acid the chloride is decomposed to a large extent into campholene, carbonic anhydride, and hydrogen chloride.

*Campholic cyanide*,  $C_{10}H_{17}O\cdot CN$  (molecular weight by cryoscopic method), prepared from the chloride and silver cyanide at  $100^\circ$ , crystallises from ether in large, white, rectangular plates, and has an odour resembling that of camphor; it melts at  $33^\circ$ , and boils at  $227^\circ$ . It is

readily hydrolysed by alkalis into its proximate constituents; with hydrochloric acid as the hydrolytic agent, the hydrogen cyanide is further hydrolysed into ammonia and carbonic oxide, or in presence of alcohol into ethylic formate.

*Dicampholyl*,  $C_{10}H_{17}O \cdot C_{10}H_{17}O$  (molecular weight by cryoscopic method), is formed by the action of sodium on campholic chloride in light petroleum; it forms lemon-yellow crystals, melts at  $90^\circ$ , and boils and decomposes at  $330-335^\circ$ . *Dicampholyl* is not hydrolysed by alcoholic potash or hydrochloric acid at  $150^\circ$ , nor is it acted on by any of the usual ketonic reagents; nevertheless, it appears to be a ketone, as it is reducible to an alcohol, the ketone being regenerated on treating this with chromic acid.

*Dicampholylic alcohol*,  $C_{10}H_{17}O \cdot C_{10}H_{18} \cdot OH$ , is formed by reducing dicampholyl with moist sodium in ethereal solution; it crystallises in small prismatic plates, and melts at  $50^\circ$ . The *acetate* (molecular weight by cryoscopic method) crystallises in small, colourless needles, and melts at  $64^\circ$ ; it is hydrolysed by alcoholic potash into its proximate constituents. J. N. W.

**Abietic acid.** By HEINRICH MACH (*Monatsh.*, 1894, 15, 627—644; compare Abstr., 1893, i, 582).—The author has previously shown (*loc. cit.*) that the so-called abietic, sylvic, and pimaric acids obtained from the resin of pine trees are one substance,  $C_{19}H_{28}O_2$ , for which the name abietic acid is retained. It crystallises on slow evaporation of its ethyl alcoholic solution in hemimorphous, monoclinic plates,  $a : b : c = 1.1866 : 1 : 0.9899$ , and gives characteristic colour reactions. A solution in dry chloroform when heated with acetic anhydride and sulphuric acid gives a purple-red coloration, which changes through violet and blue to greenish-black (compare Seifert, Abstr., 1891, i, 256, 1894, ii, 469). A solution in sulphuric acid is red. It has a specific rotatory power of  $[\alpha]_D = 66.66$ , and gives a *potassium salt*,  $C_{19}H_{27}O_2K$ , which crystallises in silky needles; an amorphous, white, *barium salt*,  $(C_{19}H_{27}O_2)_2Ba$ , which becomes yellow on exposure to air, and an *acid ammonium salt*,



which is very soluble and crystallises in drusy masses of prisms. On oxidation with potassium permanganate in alkaline solution, an *acid* having the formula  $C_{10}H_{16}O_3$  and melting at  $123^\circ$  is obtained. On oxidation with bromine water, abietic acid yields an amorphous substance which has the formula  $C_{10}H_{10}O_4$ , turns brown at  $130^\circ$ , and melts and decomposes at  $137^\circ$ .

Abietic acid is neither identical nor isomeric with Maly's pimaric acid,  $C_{20}H_{30}O_2$ , obtained from *Gallipot* and *Colophonium de Bordeaux*. The so-called metacopaivic acid appears to have the formula  $C_{15}H_{23} \cdot OH$ , and is possibly the root of the cholesterol series. On this account the author proposes to name it *metacholestol*. G. T. M.

**Amber (Succinite).** By ALEXANDER TSCHIRCH and E. AWENG (*Arch. Pharm.*, 1894, 232, 660—688).—The authors find that the portion of succinite soluble in alcohol consists principally (28 per cent. of the weight of the succinite) of *succinoabietic acid*,  $C_{30}H_{42}O_5$ ,

together with a small quantity (2 per cent.) of the borneol salt of this acid, and some sulphur. The portion (70 per cent.) of succinite insoluble in alcohol (succinin) is almost entirely composed of the succinate of a resin-alcohol to which the authors give the name *succinoresinol*. Succinoabietic acid is crystalline, soluble in alcohol and ether, insoluble in water, and melts at  $148^{\circ}$ . It forms a mon-acetyl derivative, but could not be further acetylated. When digested with alcoholic potash, it is decomposed, yielding *succinosilvic acid*,  $C_{24}H_{36}O_2$ , and *succinoabietol*,  $C_{40}H_{60}O_2$ . Succinosilvic acid is easily soluble in alcohol, ether, and glacial acetic acid, but could not be obtained in a crystalline form. It yields a white, amorphous silver salt. Succinoabietol is readily soluble in alcohol, ether, and chloroform, insoluble in light petroleum. It forms a triacetate, soluble in light petroleum. Succinoabietic acid, when fused with potash at a moderate heat, yields succinic acid. *Succinoresinol*,  $C_{12}H_{20}O$ , is a white amorphous powder soluble in a mixture of alcohol and ether and melting at  $275^{\circ}$ . It yields an *acetyl derivative* as a granular resin, soluble in alcohol and in ether.

Gedanite appears to be similar in composition to succinite, except that it is free from sulphur. It is apparently the presence of the sulphur which causes in succinite the increase of melting point, elasticity and tenacity.

Glessite contains succinoabietic acid and a succinin or a very similar compound, but was not further investigated. In it borneol seems to be replaced by a compound resembling carvol.

Allingite differs considerably from the other members of the amber group, and contains neither borneol nor succinic acid. The resin-acid also appears not to be succinoabietic acid. L. T. T.

**Commercial Thapsia Resin.** By FRANCESCO CANZONERI (*Gazzetta*, 1894, 24, ii, 437—438).—The author has isolated the following substances from commercial thapsia resin: cholesterol, ischolesterol, thapsic acid, a terpene, a camphor, angelic acid, isovaleric acid, caproic acid, caprylic acid, euphorbion, a greenish aromatic oil, a resin containing sulphur and waxy, gummy, and fatty matters, &c.; a small proportion of a substance which induces frothing and melts at  $87^{\circ}$  was also separated. The cholesterol, euphorbion, and the terpene were not found during the author's previous examination of thapsia resin (*Gazzetta*, 13, 514), and their presence is probably due to adulteration.

W. J. P.

**Sap of the Lac Tree.** By GABRIEL BERTRAND (*Bull. Soc. Chim.*, 1894, [3], 11, 717—721).—The sap of the Tonquin lac tree (*Rhus succedanea*, Linn.), which forms the basis of various kinds of lacquer, is a thick, nearly white, alkaline cream, superficially oxidisable by air to an intensely black, impervious substance, insoluble in the usual solvents.

Complete oxidation only takes place in the presence of a diastatic ferment, *laccase*, which can be separated from the other essential constituent of the sap by means of alcohol, in which it is insoluble. When precipitated by alcohol from aqueous solution, the crude laccase dries to white, opaque fragments, like gum, and is probably a mixture

of the ferment with carbohydrates, as it can be oxidised to mucic acid, and hydrolysed to galactose and arabinose.

From the portion of the sap soluble in alcohol, a substance, *laccol*, probably a polyphenol, can be precipitated by lead acetate. It is a thick oil, insoluble in water, but soluble in alcohol, &c., and is intensely irritating to the skin, as is the crude sap. *Laccol* is readily oxidisable in the air to a reddish, viscous, or resinous substance; in alkaline solution, it behaves like pyrogallol, blackening, and absorbing oxygen with such rapidity as to become hot; it reduces ferric chloride in alcoholic solution, forming a black, metallic derivative.

When *laccol* is precipitated from alcoholic solution by an aqueous solution of laccase, the white emulsion rapidly blackens from absorption of oxygen; but this does not take place if the laccase solution has been boiled, or if water alone is the precipitant. The action of laccase on gallic acid, pyrogallol, &c., is similar, the rate of absorption of oxygen being enormously increased. As the ferment has no action on starch, sugar, amygdalin, &c., it seems to be the first member of a new class of "oxidising diastases." It is probably widely distributed through the vegetable kingdom, as the author has already detected it in gum senegal and gum arabic. JN. W.

**Laccase, an Oxidising Diastase.** By GABRIEL BERTRAND (*Compt. rend.*, 1895, 120, 266—269).—The author has previously shown that the conversion of the milky juice of the lac tree into a black varnish depends partly on the action of a diastase, *laccase*, which he regarded as having hydrolysing powers analogous to those of other diastases (preceding abstract). He finds, however, that the *laccol* in the juice absorbs oxygen much more rapidly in presence of the diastase than under ordinary conditions. It seems, therefore, that *laccase* has the power of promoting oxidation, and this is confirmed by the fact that a sterilised solution of quinol containing laccase, prepared aseptically, rapidly absorbs oxygen from the air with formation of quinone and quinhydrone, although in the absence of laccase, or in presence of laccase that has been boiled for a short time, no absorption of oxygen takes place even after several days.

Pyrogallol solution in presence of laccase behaves similarly, and purpurogallin is formed, carbonic anhydride being evolved. Gallic acid and tannin are also oxidised, with liberation of carbonic anhydride. Since laccase is present in many plants, it seems not improbable that this diastase plays an important part in the respiration of plants. In the author's experiments precautions were taken to prevent the possible presence of micro-organisms. C. H. B.

**Oxidation of the Tannin of Cider Apples.** By LÉON LINDET (*Compt. rend.*, 1895, 120, 370—372).—The author has previously observed that the conditions necessary for the oxidation of the tannin of cider apples coincide with those necessary for the existence of a soluble ferment, and he concluded that a soluble ferment takes part in the oxidation (*Le Cidre*, 1893, 150). Bertrand's observations on laccase (preceding abstract) suggested that a similar diastase might be present in cider apples. When sliced or



pulped apples, or sponges moistened with the juice, are exposed to air, there is absorption of oxygen and liberation of carbonic anhydride, even if the sponges have been sterilised and the juice has been filtered through biscuit porcelain, or if oil of mustard is added. Salicylic acid and other antiseptics retard the oxidation, and chloroform and mercury compounds have the same effect, but they are known to behave similarly with diastases. The rate of oxidation varies with the alkalinity or acidity of the juice. No oxidation takes place with juice that has been boiled, and it is well known that cooked apples do not become red on exposure to air.

If apple juice is mixed with alcohol and the precipitate is suspended in water, it will cause oxidation of boiled juice. Further proof that alcohol precipitates the soluble ferment lies in the fact that apples from which the air has been pumped, and which have been crushed in alcohol, yield a juice which does not oxidise on exposure.

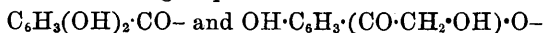
Apple juice causes the oxidation of pyrogallol to purpurogallin, but the boiled juice has not this effect.

All these facts indicate that apples contain a soluble diastase, probably a laccase, to which the oxidation on exposure to air is due; but whether the laccase acts directly, or whether it splits up the tannins into more readily oxidisable substances, has yet to be determined. The laccase is intimately associated with the tannins, and cannot be removed by merely washing with boiled water.

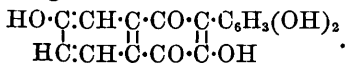
C. H. B.

**Quercetin Derivatives.** By JOSEF HERZIG (*Monatsh.*, 1894, **15**, 683—699; compare Abstract, 1888, 1309; 1890, 64; 1891, 1386; 1893, i, 413).—By the interaction of bromine and quercetin, Liebermann and Hamburger obtained a substance which they regarded as a tribromoquercetin. The author now shows that the numbers obtained by those investigators and by himself correspond much more closely with the formula for dibromoquercetin,  $C_{15}H_8Br_2O_7$ , but that the substance, on purification by recrystallisation, gradually loses bromine (compare Herzig and Pollak, this vol., i, 343). *Tetrethyl-dibromoquercetin*, obtained on bromination of tetrethylquercetin, is, on the other hand, a very stable compound, and therefore contains the bromine in the closed chain. It crystallises in yellow needles, melts at 169—173°, and does not exchange its hydroxyl groups for acetyl when heated with acetic anhydride and sodium acetate.

From the results of earlier investigations, the author regards quercetin as hydroxyfisetol, and rhamnetin as a monomethyl derivative of quercetin. Since the groups

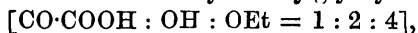


have been recognised in decomposition products of fisetol, that substance may be regarded as being formed from them by elimination of water, and as having the constitution



The quercetin group is in all probability closely related to Kostanecki's chrysin (compare Abstr., 1894, i, 93), and the connection

between fisetol and catechol is further shown by the production of diethylprotocatechuic acid and ethylresorcyglyoxylic acid,



when ethylfisetol is oxidised with potassium permanganate.

G. T. M.

**Sordidin.** By EMANUELE PATERNÒ and F. CROSA (*Gazzetta*, 1894, **24**, ii, 325—335).—The ethereal extract from *Zeora sulphurea* is a mixture of sordidin, the substance  $\text{C}_{27}\text{H}_{30}\text{O}_9$ , usnic acid, and rangiformic acid (Abstr., 1894, i, 541). Sordidin,  $\text{C}_{13}\text{H}_{10}\text{O}_8$ , which Paternò first isolated from *Zeora sordida* (*Gazzetta*, **6**, 129), has the normal molecular weight in boiling benzene, crystallises in slender, monosymmetric needles melting at  $209\text{--}210^\circ$ , and is optically inactive in solution; when boiled with alkalis, it yields a small quantity of a white crystalline acid melting at  $183\text{--}184^\circ$ . Acetic anhydride converts it into a polymeride,  $(\text{C}_{13}\text{H}_{10}\text{O}_8)_3$ , of which the molecular weight was determined by Beckmann's method, and which forms small, white, anorthic crystals melting at  $236\text{--}237^\circ$ ; a small quantity of an acetyl derivative melting at about  $198\text{--}200^\circ$  is obtained at the same time, but could not be satisfactorily purified. The benzoyl derivative,  $\text{C}_{13}\text{H}_9\text{O}_8\text{Bz}$ , melts at  $222\text{--}223^\circ$ , but could not be obtained pure owing to its admixture with the polymeride of sordidin described above; the acid melting at  $184^\circ$  is obtained on treating the above benzoyl derivative, or the polymeride, with sodium ethoxide.

Sordidin is reduced by sodium amalgam in acetic acid solution with formation of a substance,  $\text{C}_{15}\text{H}_{12}\text{O}_9$ , which crystallises in flexible, white needles melting at  $180\text{--}181^\circ$ ; the acetyl derivative,  $\text{C}_{15}\text{H}_{11}\text{O}_9\text{Ac}$ , forms lamellar crystals melting at  $149\text{--}150^\circ$ . This reduction product is accompanied by a compound crystallising in hard, red prisms melting at  $277^\circ$ .

Analyses and molecular weight determinations in boiling benzene show that the acid obtained by treating sordidin with sodium ethoxide has the composition  $\text{C}_{26}\text{H}_{28}\text{O}_{16}$ ; it crystallises in colourless needles melting at  $182\text{--}183^\circ$ , and decomposes carbonates. No oxidation products of interest were obtained either from sordidin or from this compound; the former is shown by Zeisel's method to contain one methoxy-group.

W. J. P.

**Scarlet acid.** By CARL BÖTTINGER (*Arch. Pharm.*, 1894, **232**, 698—704).—When thiocarbamide (6 grams) is rubbed in a mortar with glyoxylic acid (6.6 grams), a slight evolution of gas occurs, and a white salt is first produced which, however, rapidly changes to a tenacious, pasty mass. The colour changes first to yellow and then to red. Scarlet acid,  $\text{C}_4\text{H}_6\text{N}_4\text{S}_2\text{O}$ , when isolated from the products of the reaction, is a scarlet powder sparingly soluble in alcohol, ether, acetone, and cold water. It is sparingly soluble in hydrochloric acid, but readily soluble in sulphuric acid forming a brownish-yellow solution, which decomposes when heated. The sodium and ammonium salts have a very intense yellowish-red colour. The aluminum and lead salts form cherry-red precipitates; the silver salt a purple precipitate which gradually darkens. When the solutions of the alkali salts are boiled, the acid is decomposed, thiocarbamide being formed, ammonia

evolved, and a new substance left which is sometimes yellow and sometimes red, but yields colourless alkali salts. L. T. T.

**Chlorophylls from Lucern.** By ALEXANDRE L. ÉTARD (*Compt. rend.*, 1895, **120**, 328—331).—The author has already described one form of chlorophyll,  $\alpha$ -medicagophyll, from lucern (this vol., i, 66—67), and has shown that many of the substances commonly called chlorophylls are very complex mixtures. Chlorophylls dissolved in fused potash or in concentrated sulphuric acid are converted into brown colouring matters, which when precipitated and redissolved, although no longer green, retain the red fluorescence and the absorption characteristics of chlorophyll, and hence it would seem that there exists in plants a very stable nucleus to which various molecular groups become attached, with formation of the various chlorophylls, these rapidly undergoing chemical changes under the influence of light.

Leaves of lucern which have been exhausted with carbon bisulphide (*loc. cit.*), if treated with hot alcohol, yield a green mass; this, when separated from the brown extracts, dissolves in a small quantity of alcohol of 90°, and, after this solvent has been removed, leaves a residue which is completely soluble in ether, and therefore contains no gums, tannins, vegetable acids, &c. The product is next extracted with pentane, and the residue is treated with ether, by which it seems to be partially decomposed, a brown residue being left, whilst a green chlorophyll,  $\beta$ -medicagophyll, dissolves. It has a peculiar odour, and when dried is a green solid with a vitreous, conchoidal fracture. It is insoluble in and heavier than water, with which, however, it forms an emulsion; it dissolves immediately in dilute aqueous potash, but is reprecipitated by sodium chloride and also by acids. It reduces ammoniosilver nitrate in presence of potassium hydroxide, with production of a mirror, and hence would seem to have an aldehydic function or to be a readily decomposable glucoside.

$\beta$ -Medicagophyll has the composition  $C_{42}H_{63}NO_{14}$ , and is much more abundant in lucern than  $\alpha$ -medicagophyll. C. H. B.

**Chlorophylls.** By ARMAND GAUTIER (*Compt. rend.*, 1895, **120**, 355—356).—A question of priority. In 1877, the author showed that the chlorophyll from spinach differs from that of other plants, and notably from that of the *graminæ* in the low proportion of nitrogen and the high proportion of oxygen which it contains. It is crystallisable, contains no iron, but contains phosphorus and magnesium. In 1886, he showed that the chlorophyll from rye-grass has the composition  $C_{30}H_{48}N_2O_3$ , and that from spinach  $C_{40}H_{64}N_2O_4$ ; and this latter formula he now confirms. He also found that the chlorophyll of the male fern is remarkably sensitive to the oxygen of the air under the influence of light. Algae, fucus, and probably some higher plants contain brown, yellow, and red pigments which behave like chlorophylls, and have the power of decomposing the system  $CO_2 + H_2O$ , with liberation of oxygen. C. H. B.

**Protophyllin, Natural and Artificial.** By CLEMENZ A. TIMIRIAZEFF (*Compt. rend.*, 1895, **120**, 467—470).—The *protochlorophyll*

described by Monteverde in a recent number of *Acta Horti Petropolitani* is identical with the protophyllin described by the author, who also showed that there is no difference between the protophyllin prepared by reduction and that existing in etiolated plants (Abstr., 1886, 626, and 1889, 1236).  
C. H. B.

**Compound of Pyrroline with Hydroferrocyanic acid.** By CARLO U. ZANETTI (*Gazzetta*, 1894, **24**, ii, 373—375; compare Ciamician and Zanetti, Abstr., 1893, i, 602).—Details are given of the preparation of pyrroline ferrocyanide by the action of a hydrochloric acid solution of potassium ferrocyanide on pyrroline at a low temperature; the substance cannot be crystallised from water or alcohol, in which it dissolves, as it decomposes on heating. It is decomposed by light or by contact with air, and is converted by potash into a caseous mass.  
W. J. P.

**Coal-tar Bases.** By FELIX B. AHRENS (*Ber.*, 1895, **28**, 795—798).—The light oil from 10,000 kilos. of coal-tar was shaken with dilute sulphuric acid, and 5 kilos. of bases were so obtained. These consisted of pyridine, picoline, and lutidine, together with a fraction (400 c.c.) boiling at 160—220°; this last fraction was freed from aniline by oxidising the latter to aniline black, and was then carefully fractionated, the three fractions mentioned below being further examined. (I), boiling at 165—170°, consisted mainly of 2:4-dimethylpyridine, together with a little symmetrical trimethylpyridine, and a hitherto unknown collidine, the *platinochloride* of which, with 2H<sub>2</sub>O, darkens at 210°, decomposing finally at 255°, whilst the *aurochloride* crystallises in long needles, which, if left in the solution, change to rhomboidal crystals; it melts at 237—238°. (II), boiling at 170—180°, is mainly symmetrical trimethylpyridine. (III), boiling at 220—230°, yields a parvoline boiling at 232—234 (corr.), probably identical with the substances obtained by Greville Williams (this Journal, 1854, 97) out of the oil from Dorsetshire bituminous shale, and by Thenius (*ibid.*, 1861, 502) from coal-tar oil. It is shown to be 2:3:4:5-tetramethylpyridine, being identified by means of the tetracarboxylic acid that it yields when oxidised with permanganate; the isomeride obtained from propaldehyde-ammonia by Dürckopf and Göttisch (Abstr., 1890, 1002, where for [Me<sub>4</sub> = 1:2:3:4] read [Me<sub>4</sub> = 2:3:4:5]) must therefore have another constitution. The base is a colourless liquid, slightly soluble in water; the *platinochloride* melts and decomposes at 209—210°; the yellow *aurochloride* softens at 212°, and melts at 216—218°; the *mercurichloride* melts at 156°, and the picrate at 170—172°.  
C. F. B.

**Lead Double Salts with Organic Bases.** By WM. GOEBBELS (*Ber.*, 1895, **28**, 792—794; compare Classen and Zahorski, Abstr., 1893, 464, and Friedrich, *ibid.*, 415).—Lead tetrachloride forms a yellow, crystalline, double compound, 3PbCl<sub>4</sub>.7(C<sub>6</sub>NH<sub>7</sub>.HCl), with picoline hydrochloride; this compound dissolves in water, but lead dioxide soon separates out from the solution. It also forms a compound PbCl<sub>4</sub>.2(C<sub>6</sub>NH<sub>7</sub>.HCl), melting at 135°, with lutidine hydrochloride; if

excess of the latter is present a yellow crystalline compound,  $2\text{PbCl}_4, 5(\text{C}_7\text{NH}_9, \text{HCl})$ , melting at  $132^\circ$ , is obtained. A compound is also formed with collidine hydrochloride.

Lead dichloride unites with picoline hydrochloride to form lustrous white plates of a compound  $2\text{PbCl}_2, \text{C}_6\text{NH}_7, \text{HCl}$ , which decomposes at  $80-90^\circ$ ; with lutidine hydrochloride it unites to form a white, crystalline compound,  $2\text{PbCl}_2, \text{C}_7\text{NH}_9, \text{HCl}$ . Lead bromide unites with pyridine, forming a compound  $\text{PbBr}_2, \text{C}_5\text{NH}_5$ , which crystallises in needles. When allowed to remain in contact with pyridine, these change to rhombohedra of a compound  $5\text{PbBr}_2, 7\text{C}_5\text{NH}_5$ . Lead iodide forms with quinoline, pale yellow needles, with the composition  $\text{PbI}_2, 2\text{C}_9\text{NH}_7$ . C. F. B.

**Ethylic Nicotinate and  $\beta$ -Amidopyridine.** By FELIX POLLAK (*Monatsh.*, 1895, 16, 45—61).—Ethylic nicotinate,  $\text{C}_8\text{H}_9\text{NO}_2$ , obtained by Engler's method (*Abstr.*, 1894, i, 472), boils at  $224^\circ$  ( $6^\circ$  higher than is given by Engler), and forms the following salts:—A *hydrochloride*,  $\text{C}_8\text{H}_9\text{NO}_2, \text{HCl}$ , which crystallises in deliquescent needles and melts at  $118-120^\circ$ ; a *platinochloride*,  $\text{C}_8\text{H}_9\text{NO}_2, \text{H}_2\text{PtCl}_6$ , which crystallises in yellow needles and melts at  $161^\circ$ ; an *aurochloride*,



which crystallises in light yellow scales and melts at  $117^\circ$ ; and a readily soluble *ethiodide*. The last-named forms a *platinochloride*,  $(\text{C}_8\text{H}_9\text{NO}_2\text{Et})_2\text{PtCl}_6$ , which crystallises in small plates and melts at  $176^\circ$ ; and an *aurochloride*,  $\text{C}_8\text{H}_9\text{NO}_2\text{Et}, \text{AuCl}_4$ , which crystallises in light yellow scales, melts at  $59^\circ$ , and is converted by silver oxide into the *ethylbetaine* of *nicotinic acid*. This forms hygroscopic crystals, melts at  $84-86^\circ$ , and yields a *platinochloride*,  $(\text{C}_8\text{H}_9\text{NO}_2)_2, \text{H}_2\text{PtCl}_6$ , which crystallises in bright yellow needles, and melts at  $205^\circ$ .

On heating ethylic nicotinate with alcoholic ammonia saturated at  $-10^\circ$ , for 12 hours at  $150^\circ$ , it is converted into *nicotinamide*, which melts at  $121^\circ$  (Engler gives  $125^\circ$  as the melting point), and with potassium hypobromite yields  $\beta$ -amidopyridine,  $\text{C}_5\text{H}_6\text{N}_2$ . The latter crystallises from a mixture of benzene and light petroleum, melts at  $64^\circ$ , boils at  $250-252^\circ$ , dissolves readily in water, alcohol, ether, and benzene, and forms a *hydrochloride*,  $\text{C}_5\text{H}_6\text{N}_2, 2\text{HCl}$ , which crystallises in plates and melts at  $175^\circ$ ; a *platinochloride*,  $(\text{C}_5\text{H}_6\text{N}_2)_2, \text{H}_2\text{PtCl}_6$ , which melts and decomposes at  $225^\circ$ , and an *aurochloride*,  $\text{C}_5\text{H}_6\text{N}_2, \text{HAuCl}_4$ , which crystallises in dark-red needles and decomposes and evolves gas at  $218^\circ$ . On the addition of potassium nitrite to a solution of  $\beta$ -amidopyridine in dilute sulphuric acid,  $\beta$ -hydroxypyridine, which melts at  $126.5^\circ$ , is obtained.

In the preparation of  $\beta$ -amidopyridine, a substance which melts at  $100^\circ$ , contains bromine, and is probably *bromamidopyridine*, is formed as a bye-product. If a relatively small quantity of potash is used in the preparation, less amidopyridine is formed, and the liquid, on shaking with ether, yields a substance which crystallises in scales, melts at  $129-131^\circ$ , has an odour of iodoform, and is isomeric with nicotinamide. G. T. M.

**Quinoline in Brown-coal Tar.** By OSCAR G. DOEBNER (*Arch. Pharm.*, 1894, **232**, 691—693).—The author has isolated quinoline from the fraction of brown-coal tar boiling at 240—245°. Other quinoline and pyridine derivatives are also present. L. T. T.

**2 : 4-Dichloroquinoline.** By ADOLPH CLAUS and ALFRED AMMELBURG (*J. pr. Chem.*, 1895, [2], **51**, 415—422; compare *Abstr.*, 1894, i, 473, 553).—2 : 4-Dichloroquinoline is prepared by the usual method from 3 : 5-dichloraniline; it crystallises in colourless, lustrous prisms or aggregates of needles, melts at 116—117°, and sublimes in needles. Its salts are prepared by dissolving it in strong acids; the *hydrochloride* melts at 216°, and the anhydrous *sulphate* at 162°; the *dichromate* melts and decomposes at 159°; the *platinochloride* is described; the *methiodide* melts at 255—257°; the *methochloride* and its *platinochloride* were prepared.

1 : 2 : 4-Nitrodichloroquinoline crystallises in tablets or prisms, melts at 168·5°, and dissolves freely in ether and chloroform, but only sparingly in cold alcohol; no salts and no methiodide can be prepared; the *platinochloride* decomposes and melts at 255°. The corresponding *amido*-derivative crystallises in brilliant, colourless prisms, which speedily become coloured on exposure to light; it melts at 125°, and dissolves freely in alcohol, ether, and chloroform; its *hydrochloride*,  $C_9H_6Cl_2N \cdot HCl$ , forms red needles, melts and decomposes at 183°, and is dissociated by water; the *platinochloride* and *methiodide* (m. p. 154°) are described.

By diazotising the above amidodichloroquinoline, 1 : 2 : 4-trichloroquinoline is obtained; this crystallises in prisms and melts at 150°.

A. G. B.

**Constitution of the Hydroquinolines.** By GIACOMO CIAMICIAN and G. BOERIS (*Gazzetta*, 1894, **24**, ii, 299—310).—The indolic properties of dihydrotrimethylquinoline (Ferratini, *Abstr.*, 1894, i, 96) are shown by the behaviour of its acetyl derivative towards benzaldehyde; a *cinnamoyldihydrotrimethylquinoline*,  $C_{21}H_{21}NO$ , is thus obtained, which crystallises in beautiful, orange-yellow, rectangular plates melting at 152—153°, and dissolves in most organic solvents.

On distilling dihydrotrimethylquinoline hydriodide, a mixture of methylic iodide, trimethylindole and dihydrotrimethylquinoline is obtained; the latter crystallises in the orthorhombic system,  $a : b : c = 1.3558 : 1 : 0.5984$ . Trimethylindole is readily converted into dihydrotrimethylquinoline hydriodide by heating with methylic iodide at 100°.

A discussion of the constitutions of the quinolines and indoles is given. W. J. P.

**Action of Phosphoric Anhydride on Benzylideneacetone-oxime.** By CARL GOLDSCHMIDT (*Ber.*, 1895, **28**, 818—819).—Benzylideneacetoneoxime, when mixed with infusorial earth and treated with phosphoric anhydride, yields isoquinoline. It appears therefore that, as in the case of cinnamaldehyde (*Abstr.*, 1894, i, 552), intramolecular change occurs. A. H.

**Cyanide and Carboxylic acid Derived from Isoquinoline.** By BERTHOLD JEITELES (*Monatsh.*, 1894, 15, 807—820).—*Cyanoisoquinoline* is obtained on distilling in a stream of hydrogen a mixture of the dried sodium salt of Hoegewerff and van Dorp's isoquinolinemonosulphonic acid with potassium ferrocyanide. It crystallises from water in yellow needles, melts at 135°, and, when heated with hydrochloric acid at 150—160°, yields the *hydrochloride of isoquinolinecarboxylic acid*,  $C_9NH_6 \cdot COOH, HCl + 2H_2O$ . The latter crystallises in needles and forms a red solution, which shows a green fluorescence. The free acid,  $C_{10}H_7NO_2$ , is sparingly soluble in water, crystallises in yellow needles, commences to blacken at 247—250°, and melts at 272°. The *nitrate* crystallises in needles, gives a yellow solution showing a green fluorescence, and melts and decomposes at 218—220°. The *picrate* melts at 212—213°.

On oxidation in neutral solution with potassium permanganate, isoquinolinecarboxylic acid is converted into hemimellitic acid. The carboxyl group is therefore in the *ortho*- or *ana*-position.

G. T. M.

**$\beta$ -Cyano- $\gamma$ -phenylpseudocarbostyrl.** By ICLIO GUARESCHI (*Chem. Centr.*, 1894, ii, 211).— $\beta$ -Cyano- $\gamma$ -phenylpseudocarbostyrl,  $NH < \begin{matrix} C_6H_4 \cdot CPh \\ CO - \overset{||}{C} - CN \end{matrix}$ , is obtained by the action of ethylic cyanacetate on orthamidobenzophenone; it forms colourless needles, melts at 267°, and volatilises and sublimes at a higher temperature; it is isomeric with Gabriel and Neumann's 3 : 4-phenylcyanisocarbostyrl.

D. A. L.

**Hydroxamic Acids and Hydroxyfurfurazane Derivatives.** By ARTHUR HANTZSCH and J. URBAHN (*Ber.*, 1895, 28, 753—766; compare *Abstr.*, 1894, i, 274).—Ethylic succinate and hydroxylamine, in presence of alkalis or ammonia, react, succinamide and succinamine-hydroxamic acid being formed; the latter could not be isolated on account of its great solubility, but was recognised by means of the ferric chloride reaction, and the production of the *tetracetate*,  $C_2H_4[C(OAc):NOAc]_2$ , which crystallises in long needles and melts at 130°. *Oxaldi-hydroxamic tetracetate*,  $OAc \cdot N : C(OAc) \cdot C(OAc) : N \cdot OAc$ , crystallises in cubical crystals, melts at 141°, and resembles the preceding compound. *Malondi-hydroxamic acid* forms an acetate with difficulty; it melts at 65—67°, and was only obtained in small quantity.

*Ammonium oxazolonehydroxamate*,  $CO < \begin{matrix} CH_2 \cdot C(OH) \cdot N \cdot OH, NH_3 \\ O - N \end{matrix}$ ,

is prepared from ethylic oxalate, hydroxylamine, and ammonia; it crystallises in long prisms, melts and decomposes at 156—160°, and is very readily soluble. The recently prepared salt is neutral, but speedily becomes slightly acid; it becomes successively yellow and red in air, gives a deep red coloration with ferric chloride, and reduces alkaline silver solutions but not Fehling's solution. The *copper salt* is green; the *silver salt* yellow; both these and the *lead salt* dissolve in acetic acid. The acid could not be isolated. *Cyanoximidoacetic*

acid,  $\text{CN}\cdot\text{C}(\text{NOH})\cdot\text{COOH}, \frac{1}{2}\text{H}_2\text{O}$ , is prepared by the action of nitrous acid on the preceding compound, and has been previously obtained by Wolff; it gives a yellow, not red, coloration with ferric chloride.

*Hydroxyfurazaneacetic acid*,  $\text{O} < \begin{array}{c} \text{N}:\text{C}:\text{OH} \\ | \\ \text{N}:\text{C}:\text{CH}_2\cdot\text{COOH} \end{array}$ , is formed by heating ammonium oxalzonehydroxamate with alkali, or directly from ethylic oxalate, hydroxylamine, and soda; it crystallises in colourless prisms or plates, and melts at  $158^\circ$ . The yield is 25 per cent. of the ethylic oxalate employed. The acid is bibasic, does not reduce ammoniacal silver solution, gives a yellow coloration with ferric chloride, and is extremely stable; its molecular weight was determined cryoscopically and by the boiling point method. The ammonium salt,  $\text{C}_4\text{H}_4\text{N}_2\text{O}_4\cdot 2\text{NH}_3$ , crystallises in short, truncated prisms, and melts and decomposes at  $174^\circ$ . The calcium salt,  $\text{C}_4\text{H}_2\text{N}_2\text{O}_4\cdot\text{Ca} + \text{H}_2\text{O}$ , crystallises in rhombic prisms. The silver and lead salts are sparingly soluble, the former is crystalline and explodes when heated; the chloride has also been prepared.

*Hydroxyfurazane-carboxylic acid*,  $\text{O} < \begin{array}{c} \text{N}:\text{C}:\text{OH} \\ | \\ \text{N}:\text{C}:\text{COOH} \end{array}$ , is prepared by the oxidation of hydroxyfurazanacetic acid with potassium permanganate in alkaline solution; it crystallises in prisms, melts at  $175^\circ$ , has no action on ferric chloride at ordinary temperatures, but when previously warmed with alkali gives a red coloration indicating a resolution of the closed chain. The acid is stable towards hydrochloric acid; with potassium permanganate in acid solution, cyanacetic acid is formed. The ammonium salt,  $\text{C}_3\text{N}_2\text{O}_4(\text{NH}_4)_2$ , crystallises in hexagonal needles, and melts at about  $195^\circ$ . The barium salt,  $\text{C}_3\text{N}_2\text{O}_4\cdot\text{Ba}$ , is very sparingly soluble, and melts and decomposes above  $200^\circ$ .

Hydroxyimidopropionamide,  $\text{NOH}:\text{CMe}:\text{CO}\cdot\text{NH}_2$ , is formed from ethylic pyruvate, hydroxylamine, and ammonia. Ethylic pyruvate (1 mol.) and hydroxylamine (2 mols.) yield ethylic hydroxyimidopropionamide, which, like the amide, gives no coloration with ferric chloride; when boiled with an alkali, hydroxyimidopropiohydroxamic acid is formed; further boiling alone or with an alkali yields only hydroxyimidopropionic acid.

J. B. T.

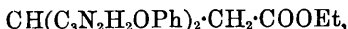
**Antipyrine.** By FRIEDRICH STOLZ (*Ber.*, 1895, **28**, 623—634).—This paper is devoted to a detailed criticism of v. Rothenburg's reasons for regarding 1 : 3-phenylpyrazolone, which melts at  $154^\circ$ , as the 1 : 5-derivative (this vol., i, 303), a view which the author holds to be erroneous.

1 : 5-Phenylpyrazolidone,  $\text{CO} < \begin{array}{c} \text{NPh}\cdot\text{NH} \\ | \\ \text{CH}_2-\text{CH}_2 \end{array}$ , is obtained by the action of ethylic  $\beta$ -iodopropionate on sodium formylphenylhydrazine dissolved in xylene, and subsequent hydrolysis of the product (German Patent, 74,858); it melts at  $78^\circ$  (compare Abstr., 1894, i, 145). The calculated quantity of ferric chloride converts it into 1 : 5-phenylpyrazolone, whilst excess of the reagent gives rise to pyrazolone blue.



*Benzylidene-bis-3 : 1 : 5-methylphenylpyrazolone* is obtained by heating a mixture of methylphenylpyrazolone and benzaldehyde with alcoholic hydrochloric acid; it forms lustrous crystals, and melts at 248°. The action of diazobenzene chloride converts it into 3 : 1 : 4-methylphenylbenzeneazopyrazolone, which melts at 155°.

*Ethylic bis-1 : 5-phenylpyrazolone-4-β-propionate*,



is obtained by heating the hydrazone of ethylic formylacetate with toluene (German Patent, 55,117); it melts at 173—174°. The *platino-chloride* is crystalline. The *acid* is formed when the ethylic salt is hydrolysed.

Ethylic 3 : 5 : 1-dimethylphenylpyrazole-4-carboxylate is obtained by the action of acetic chloride on the hydrazone of ethylic acetoacetate and subsequent treatment of the product with alcoholic potash. It melts at 196—198°, and the ethylic salt is identical with Walker's 5 : 3 : 1-ethoxymethylphenylpyrazole. When this method of preparation is adopted, 3 : 1 : 5-methylphenylpyrazolone is formed at the same time.

M. O. F.

**Constitution of the Phenylpyrazoles.** By LUDWIG KNORR (*Ber.*, 1895, 28, 688—696).—The author maintains, in reply to the criticism of Rothenburg (this vol., i, 303) and Buchner (this vol., i, 192), that the phenylpyrazole melting at 78° is the 3- or 5-compound. The derivative melting at 228°, on the other hand, is the 4-compound. Rothenburg's statement that this substance is formed by the action of hydrazine hydrate on benzoylaldehyde is inaccurate, the sole product of the reaction being the phenylpyrazole which melts at 78° (see following abstract). The constitution of 4-phenylpyrazole is proved by the fact that it can be synthetically prepared by a method which admits of no doubt as to the constitution of the resulting pyrazole (next page). Attempts to prepare 4-phenylpyrazole by other methods failed. Ethylic oxalate condenses with benzyl methyl ketone to form *phenyldiketopentoic acid*,  $\text{COOH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{Ph}$ , which is converted by hydrazine hydrate into 3 : 5-benzylpyrazolecarboxylic acid, and does not form the wished for isomeride,  $\text{COMe} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{COOH}$ , from which a 4-substituted phenylpyrazole derivative might have been obtained. It was also found impossible to prepare a pure 4-pyrazolecarboxylic acid from 4-nitropyrazole by means of the diazo-reaction.

A. H.

**Condensation of Benzoylaldehyde with Hydrazine.** By LUDWIG KNORR (*Ber.*, 1895, 28, 696—698; compare foregoing abstract).—A careful examination of the reaction between benzoylaldehyde and hydrazine shows that the product consists entirely of the phenylpyrazole, which melts at 78°, and is, according to the author, the 3- or 5-derivative. Rothenburg's statement that the pyrazole which melts at 228° is thus formed, is therefore inaccurate. A number of new derivatives of the compound has also been prepared. The *picrate* melts at 170—171°. The *carbamide* crystallises

in needles, and melts at 137—139°. 4-Bromophenylpyrazole melts at 116—117°. Nitrophenylpyrazole melts at 192—193°. 1-Methylphenylpyrazole boils at 280—281°, and forms a *picrate*, which melts at 130—132°, and a *platinochloride*, which crystallises in plates melting at 190°. The *methiodide* of the same base melts at 156—157°, whilst the *platinochloride* of the corresponding methochloride forms orange-coloured prisms, and decomposes at 224°. A. H.

**Formation of 4-Phenylpyrazole.** By LUDWIG KNORR (*Ber.*, 1895, 28, 699—701; compare preceding page).—Isopropyl benzyl ketone readily condenses with ethylic formate to produce *hydroxymethylenebenzyl isopropyl ketone*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CPh}\cdot\text{CH}\cdot\text{OH}$ , which is a colourless oil. When treated with hydrazine hydrate in ethereal solution, 3:4-isopropylphenylpyrazole is formed, which melts at 99—100°; the *hydrochloride* decomposes at 214—215°. On oxidation, 4:3-phenylpyrazolecarboxylic acid is formed; this crystallises in lustrous plates, and melts and loses carbonic anhydride at 253—254°. It is accompanied by a small amount of *phenylpyrazole-dimethylcarbinol*,  $\text{CH}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix}\text{C}\cdot\text{CMe}_2\cdot\text{OH}$ , which melts at 129—130°. 4-Phenylpyrazole is formed when the carboxylic acid is heated at 270°. The substance thus obtained melts at 228°, and is identical with the compound described by Buchner. A. H.

**Constitution of Phenylpyrazolone.** By LUDWIG KNORR (*Ber.*, 1895, 28, 701—705; compare the following abstract).—The substance described by Walker (*Abstr.*, 1894, i, 475) as 5:3:1-ethoxymethylphenylpyrazole is probably identical with ethylic 3:5:1-dimethylphenylpyrazole-4-carboxylate, previously described by the author (*Abstr.*, 1887, 678), whilst Walker's hydroxymethylphenylpyrazole, obtained by hydrolysis from the first compound, is the corresponding free acid. This removes the ground upon which Rothenburg has founded his criticism of the author's view that the phenylpyrazolone melting at 118° is the 1:5-compound. The formulæ proposed by Rothenburg for the isomeric benzoyl derivatives of the technical pyrazolone are also inaccurate. A. H.

**Derivatives of the Phenol-form of 3:1-Ethylphenyl-5-pyrazolone.** By LUDWIG KNORR (*Ber.*, 1895, 28, 706—714; compare the foregoing abstract).—The technical pyrazolone (3:1-methylphenyl-5-pyrazolone) yields three isomeric series of substitution compounds, derived from the methylene-, imine- and phenol-form respectively. The derivatives of the phenol-form may be prepared by direct synthesis from the corresponding ethereal acetoacetate or from the technical pyrazolone by substitution. They are true pyrazole derivatives; their salts are dissociated by water, and they are reduced by alcohol and sodium to pyrazolines. Like the pyrazoles they are devoid of any antipyretic action on the organism. 5:3:1-Ethoxymethylphenylpyrazole has previously been prepared by Freer (*Abstr.*, 1892, 953) and by Stolz (private communication).

It boils at 293—295°, and melts indefinitely at 40°. The *platinochloride* crystallises in characteristic groups of needles, and melts at 195°. When heated with hydrochloric acid at 160—170°, it is decomposed with formation of the technical pyrazolone and methylketole. On treatment with methylic iodide, followed by aqueous soda, the pyrazole is converted into antipyrine, whilst it is reduced by alcohol and sodium to 1:3-phenylmethylpyrazoline.

5:3:1-Methoxymethylphenylpyrazole may be obtained from methylic acetoacetate or by the methylation of technical pyrazolone. It boils at 247—248° (225 mm.), and forms a *platinochloride* which decomposes at 180—182°. 5:3:4:1-Methoxydimethylphenylpyrazole boils at 244—245° (225 mm.), and yields 3:4:1-dimethylphenylpyrazolone when treated with hydrochloric acid, whilst it is converted by methylic iodide into 4-methylantipyrine.

5-Hydroxyethoxy-3:1-methylphenylpyrazole is formed, along with the corresponding antipyrine, by the action of ethylenic chloride and sodium ethoxide on the technical pyrazolone (Aldrich, Dissert., Jena, 1892). It crystallises with 1 mol. H<sub>2</sub>O, melts, when anhydrous, at 53—54°, and has the characteristic properties of its class. 4-Bis-5:2:1-methoxymethylphenylpyrazole is formed by the methylation of bis-methylphenylpyrazolone, and melts at 186—187°. The condensation product of ethylic acetoacetate with technical pyrazolone seems also to be a derivative of the phenol-form of pyrazolone.

The author proposes the term *double tautomerism* for cases in which three series of isomeric compounds are derived from a single parent substance.

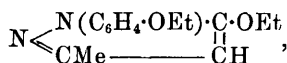
Further details of the experimental work will shortly be published.  
A. H.

**The Aromatic Character of the Pyrazoles.** By LUDWIG KNORR (*Ber.*, 1895, **28**, 714—719).—The close analogy which has been pointed out between the derivatives of pyrazole and of benzene is strengthened by the following facts. Pyrazole is converted by fuming sulphuric acid into a sulphonic acid, melting at 330—335°. The mono-halogen derivatives behave in the same manner as the mono-halogen benzene derivatives, and 4-nitropyrazole is converted by reduction into a base which has all the characteristic properties of the aromatic bases, yields diazo-salts, and forms azo-colouring matters. At the same time, pyrazole possesses the properties of a weak secondary base. Thus, 1-methylpyrazole, which boils at 126—127°, is formed by heating silver pyrazole with methylic iodide. Pyrazole also yields a 1-benzoylpyrazole, boiling at 281°; a 1-acetyl derivative, boiling at 155—156°; a 1-urethane, boiling at 213°; and a 1-carbamide, melting at 136·5°. Full details of these compounds will be subsequently published.

4:1:3:5-Nitrotrimethylpyrazole (*Abstr.*, 1894, i, 545) melts at 56—57° and boils at 245—247° (202 mm.). On reduction, it is converted into the *amido-compound*, which melts at 102—104°, is readily soluble in water and alcohol, and reduces silver oxide. The *hydrochloride* has the composition C<sub>6</sub>H<sub>11</sub>N<sub>3</sub>·2HCl. It is converted by the action of nitrous acid into a diazo-salt, which at once yields azo-colouring matters with phenols, and also reacts with the technical

pyrazolone to form a *hydrazone* of 3:1-methylphenyl-4-keto-5-pyrazolone,  $\text{PhN}-\text{CO} \begin{matrix} \text{N}:\text{CMe} \end{matrix} > \text{C}:\text{N} \cdot \text{NH} \cdot \text{C} \begin{matrix} \text{CMe} \cdot \text{NMe} \\ \text{CMe}:\text{N} \end{matrix}$ , which crystallises in orange-coloured needles melting at  $156^\circ$ . The diazo-salt is very stable in aqueous solution, and only decomposes gradually when its solution is heated at  $120^\circ$ . A boiling solution of potassium iodide converts it into 4-iodotrimethylpyrazole, which melts at  $75^\circ$ . A. H.

**1:3:5-Parethoxyphenylmethylethoxypyrazole.** By FRIEDRICH STOLZ (*Ber.*, 1895, **28**, 635—639; compare *Abstr.*, 1892, 1080).—When parethoxyphenylhydrazine is warmed with ethylic acetate, 1:3:5-parethoxyphenylmethylpyrazolone is formed (*loc. cit.*). 1:3:5-Parethoxyphenylmethylethoxypyrazole,



is produced at the same time, and is obtained on evaporating the ethereal solution of the mixed bases after agitation with aqueous soda; it crystallises in yellowish prisms, and melts at  $84^\circ$ . It resists the action of boiling aqueous soda, hydrochloric acid, ferric chloride, and cupric acetate; the *hydrochloride* is decomposed by water. When heated with methylic iodide and methylic alcohol, it is converted into 1:2:3-parethoxydimethylpyrazolone (parethoxyantipyrine).

1:3:5-*Parahydroxyphenylmethylethoxypyrazole* is obtained by heating 1:3:5-parethoxyphenylmethylethoxypyrazole with concentrated hydrochloric acid for three hours at  $150^\circ$ ; it crystallises in colourless plates, and melts at  $195^\circ$ . The substance dissolves in acids and alkalis, but is insoluble in alkali carbonates.

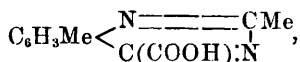
1:3:5-*Parahydroxyphenylmethylpyrazolone* is produced when the foregoing compound is heated with hydrochloric acid at  $150^\circ$  for two hours; it is also formed when 1:3:5-parethoxyphenylmethylpyrazolone is treated in the same manner. This substance melts at  $230^\circ$ , and dissolves in acids and alkalis; nitrous acid gives rise to a red *isonitroso*-derivative. When 1:3:5-phenylmethylpyrazolone is heated with hydrochloric acid for three hours, a small quantity of  $\alpha$ -methylindole is formed, but the greater part of the pyrazolone derivative remains unchanged.

1:3:4:5-*Parethoxyphenylmethylnitroethoxypyrazole* is obtained by the action of nitrous acid on 1:3:5-parethoxyphenylmethylethoxypyrazole. It forms lustrous crystals, and melts at  $119^\circ$ .

M. O. F.

**Phenometadiazine Derivatives.** By AUGUST BISCHLER and H. P. MUNTENDAM (*Ber.*, 1895, **28**, 723—738; compare this vol., i, 250).—*Acetylparamethylisatic acid*,  $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{COOH}$ , is prepared by the action of soda on acetylparamethylisatin, and melts at  $166^\circ$ .

$\beta$ -*Methylparatoluometadiazine- $\alpha$ -carboxylic acid*,



obtained by the action of alcoholic ammonia on the preceding compound, crystallises with  $2\text{H}_2\text{O}$  in pale yellow plates, and melts at  $160$ — $161^\circ$ , carbonic anhydride being evolved. The compound is readily soluble in water, mineral acids, glacial acetic acid, alkalis, and alkali carbonates. The *ammonium* salt crystallises in reddish needles and decomposes above  $120^\circ$ . The *silver* salt crystallises with  $4\text{H}_2\text{O}$  in large, yellow, transparent prisms. The *mercurous*, *barium*, and *copper* salts are amorphous and sparingly soluble. The *methylic* salt crystallises in plates, the *ethylic* salt in large, yellow, flat prisms; they melt at  $96^\circ$  and  $71^\circ$  respectively. The *ethylic hydrochloride*,  $\text{C}_{10}\text{H}_9\text{N}_2\cdot\text{COOEt}\cdot\text{HCl}$ , is sparingly soluble in ether. The *platinochloride* is reddish-yellow, the *picrate* yellow; both are sparingly soluble and pulverulent. The *amide*,  $\text{C}_{10}\text{H}_9\text{N}_2\cdot\text{CO}\cdot\text{NH}_2$ , is prepared by the action of alcoholic ammonia on the above ethylic salt or on acetylparamethylisatamide, it crystallises in long, colourless needles, and melts at  $212^\circ$ . Attempts to prepare the nitrile were unsuccessful.

*$\beta$ -Methylparatoluometadiazine*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CH}:\text{N} \end{smallmatrix}\rangle$ , is formed by heating the above ammonium salt with calcium oxide, but is most readily prepared by the distillation of the carboxylic acid; it crystallises in large, pale yellow plates, melts at  $79^\circ$ , and boils at  $255^\circ$  (726 mm.). The *hydrochloride* is pale yellow, pulverulent, and decomposes at about  $180^\circ$ . The *platinochloride* crystallises in orange-coloured, the *picrate* in golden, concentric needles; the latter melts at  $145^\circ$ .

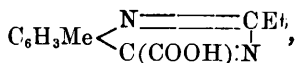
*$\alpha$ -Hydroxy- $\beta$ -methylparatoluometadiazine*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{N}=\text{CMe} \\ \text{C}(\text{OH})\cdot\text{N} \end{smallmatrix}\rangle$ , is formed by the oxidation of the hydrocarbon with chromic anhydride, and has been previously prepared by Niementowski from orthamidoparatoluamide and acetic anhydride.

*Propionylparamethylisatin*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{N}(\text{COEt}) \\ \text{CO} \end{smallmatrix}\rangle\text{CO}$ , formed from paramethylisatin and propionic anhydride, crystallises in golden plates, and melts at  $143^\circ$ . *Propionylparamethylisatic acid*,



is prepared like the acetyl derivative, crystallises in small, colourless prisms, and melts at  $161$ — $162^\circ$ .

*$\beta$ -Ethylparatoluometadiazine- $\alpha$ -carboxylic acid*,



is obtained by the action of alcoholic ammonia on the preceding compound, and melts at  $154^\circ$ , carbonic anhydride being evolved. The *silver* salt crystallises in colourless plates; the *ammonium* salt is deposited in long, white, concentric needles, melting at  $146^\circ$ . Various sparingly soluble metallic salts have also been obtained. The *methylic* salt crystallises in small needles, and melts at  $30^\circ$ . The *ethylic* salt, which was not completely purified, was obtained as a pale yellow, oily liquid; it boils under reduced pressure without decompo-

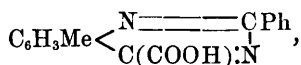
sition. The *amide* crystallises in long, colourless needles, melts at  $168^{\circ}$ , and was prepared from *propionylparamethylisatic amide*,  $\text{COEt}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CONH}_2$ , which also crystallises in needles, and melts at  $186^{\circ}$ .

*$\beta$ -Ethylmetaparatoluodiazine*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{N}=\text{C} & \text{Et} \\ | & | \\ \text{CH} & \text{N} \end{smallmatrix}\rangle$ , is formed from the carboxylic acid or the ammonium salt, crystallises in yellow needles, melts at  $38^{\circ}$ , and boils at  $265\text{--}266^{\circ}$  (730 mm.). The *platinochloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ , is greyish-yellow.

The following phenyl derivatives were obtained in a similar manner to the preceding methyl and ethyl compounds.

*Benzoylparamethylisatin*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{NBz} \\ | \\ \text{CO} \end{smallmatrix}\rangle\text{CO}$ , crystallises in yellowish-green needles, and melts at  $193^{\circ}$ . *Benzoylparamethylisatic acid*,  $\text{NHBz}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{COOH}$ , melts at  $183^{\circ}$ .

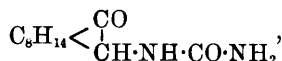
*$\beta$ -Phenylparatoluometadiazine- $\alpha$ -carboxylic acid*,



is colourless, almost insoluble in water, and melts at  $155^{\circ}$ . The *silver salt* is pulverulent. The *ammonium salt* crystallises in colourless, silky, lustrous, concentric needles, and melts at  $161^{\circ}$ . The *ethylic salt* is deposited in prisms, and melts at  $121^{\circ}$ . The *amide* crystallises in concentric needles, which melt at  $256^{\circ}$ ; it is prepared from *benzoylparamethylisatic amide*,  $\text{NHBz}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CONH}_2$ , which forms pale green needles melting at  $219^{\circ}$ .

*$\beta$ -Phenylparatoluometadiazine*,  $\text{C}_6\text{H}_3\text{Me}\langle\begin{smallmatrix} \text{N}=\text{C} & \text{Ph} \\ | & | \\ \text{CH} & \text{N} \end{smallmatrix}\rangle$ , obtained from the carboxylic acid, crystallises in small, straw-coloured plates, melts at  $133^{\circ}$ , boils above  $360^{\circ}$ , and has no smell. The *hydroxyl-derivative* is yellow and sparingly soluble. J. B. T.

**Imidazolones and their Decomposition Products.** By HANS RUPE (*Ber.*, 1895, **28**, 777—780).—Amidocamphorcarbamide,



(*Abstr.*, 1894, i, 241), when heated with zinc chloride or with strong sulphuric acid, yields *camphorimidazolone*,  $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix} \text{C}\cdot\text{NH} \\ | \\ \text{C}\cdot\text{NH} \end{smallmatrix}\rangle\text{CO}$ , or perhaps  $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix} \text{C}=\text{N} \\ | \\ \text{CH}\cdot\text{NH} \end{smallmatrix}\rangle\text{CO}$ . This crystallises in tiny, white needles, and melts above  $320^{\circ}$ ; it resembles phenylimidazolone (*Abstr.*, 1894, i, 241; this vol., i, 218) in its properties. It does react with acetic anhydride in the presence of sodium acetate, but the product is not a simple acetyl derivative. C. F. B.

**Dithiourazole and its Derivatives.** By MARTIN FREUND and HANS IMGART (*Ber.*, 1895, **28**, 946—957; compare *Abstr.*, 1894, i, 97

and 477).—Dithiourazole,  $\text{NH} \begin{smallmatrix} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ , is obtained by the action of boiling hydrochloric acid on hydrazodicarbonthiamide (*loc. cit.*), which loses 1 mol. of hydrogen sulphide under these conditions. It crystallises from water and dilute alcohol in colourless, rhombic prisms; it sinters at  $240^\circ$  and melts at  $245^\circ$ . The *acetyl* derivative crystallises from water in plates; at  $250^\circ$  it becomes brown, and melts at  $300^\circ$ , undergoing decomposition. It dissolves in dilute alkalis, and is precipitated from solution on the addition of acids. The *azo*-compound,  $\text{C}_2\text{HN}_3\text{S}_2$ , is formed on oxidising dithiourazole with ferric chloride or hydrogen peroxide; it crystallises in slender, yellow plates, and melts at  $244\text{--}245^\circ$ . On acidifying the alkaline solution of this substance, dithiourazole is regenerated.

Imidothiourazole,  $\text{NH} \begin{smallmatrix} \text{CS} \text{---} \text{NH} \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$ , is also formed when hydrazodicarbonthiamide is heated with hydrochloric acid, and, owing to its basic properties, can easily be separated from dithiourazole. It crystallises from ether in colourless prisms, which sinter at  $215^\circ$  and melt at  $221\text{--}223^\circ$  (compare *loc. cit.*). The *hydrochloride* forms colourless crystals, which contain  $1\text{H}_2\text{O}$ . The *diacetyl* derivative crystallises from hot water in slender, white needles; it becomes brown at  $291^\circ$ , and does not melt below  $315^\circ$ . It resists the action of acids and alkalis, and is scarcely soluble in cold water or alcohol.

*Hydrazodicarbonthioethylamide*,  $\text{N}_2\text{H}_2(\text{CS} \cdot \text{NHEt})_2$ , is prepared by heating hydrazine sulphate (1 mol.) and the calculated quantity of sodium carbonate with ethylthiocarbimide (2 mols.) dissolved in alcohol; it crystallises in lustrous, colourless leaflets, sinters at  $190^\circ$ , and decomposes at  $270^\circ$ . It undergoes no change when dissolved in cold concentrated sulphuric acid.

*Ethyl dithiourazole*,  $\text{NEt} \begin{smallmatrix} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ , is obtained from the foregoing substance by the action of boiling hydrochloric acid. It crystallises from water in aggregates of colourless prisms, and melts at  $140^\circ$ . The *sodium* salt forms colourless prisms; it dissolves in alcohol, and melts at  $170^\circ$ . The *silver* salt is colourless, and becomes black when heated. Ethyl dithiourazole is not desulphurised when an aqueous solution of the sodium salt is heated with mercuric oxide, and no silver sulphide is formed when the ammonium salt is heated with ammoniacal silver solution. The *nitroso*-compound is obtained on adding concentrated nitric acid to the hot, aqueous solution; it is also formed when dilute hydrochloric acid is added to the mixed solutions of sodium nitrite and the sodium salt of ethyl dithiourazole. The compound crystallises from alcohol in pale yellow needles, and melts at  $118\text{--}120^\circ$ ; it gives Liebermann's reaction. The *azo*-compound,  $\text{C}_4\text{H}_5\text{N}_3\text{S}_2$ , is formed on adding a concentrated solution of potassium nitrite to the hot, aqueous solution of ethyl dithiourazole. It crystallises in yellow plates, and melts at  $198^\circ$ ; when treated with alcoholic ammonium sulphide, it yields the original substance. On adding a freshly-prepared solution of diazobenzene chloride to an ice-cold solution of ethyl dithiourazole in excess of sodium carbonate, a

yellow substance is precipitated, which soon becomes greyish-brown ; while in a moist condition it explodes when spread on a porous tile.

*Methylethylthiourazole* is obtained by heating an alcoholic solution of ethylthiourazole with sodium ethoxide (1 mol.) and methylic iodide (1 mol.) for two hours ; it crystallises in colourless leaflets, and melts at 88°.

*Ethylimidoethylthiourazole*,  $\text{NEt} < \begin{smallmatrix} \text{CS} \text{---} \text{NH} \\ \text{C}(\text{NEt}) \cdot \text{NH} \end{smallmatrix}$ , is formed, together with ethylthiourazole, when hydrazodicarbonthioethylamide is treated with boiling hydrochloric acid. It crystallises from water in colourless prisms, and melts at 173°. The *hydrochloride* contains  $1\text{H}_2\text{O}$ , and melts at 98°. The *nitroso*-derivative crystallises from alcohol in lustrous, golden leaflets, sinters at 135°, and melts at 145°. The *diacetyl* derivative forms white needles, and melts at 165°. When ethylimidoethylthiourazole is heated with methylic iodide at 100°, the *hydriodide* of a monomethylated base is formed ; it crystallises from alcohol in white needles, and melts at 181°.

*Phenylthiourazole*,  $\text{NPh} < \begin{smallmatrix} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ , is obtained by the action of hydrochloric acid on hydrazodicarbonthiophenylamide. It crystallises in colourless leaflets, sinters at 205°, and melts at 219°. The *azo*-compound,  $\text{C}_6\text{H}_5\text{C}_3\text{S}_2$ , forms reddish-yellow plates, sinters at 230°, and melts at 240°. The *acetyl* derivative crystallises in lustrous, white leaflets, sinters at 240°, and melts at 252°. When treated with hydrogen peroxide or nitrous acid, the alcoholic solution yields a *compound*,  $\text{C}_{12}\text{H}_{16}\text{N}_6\text{S}_4\text{O}_2$ , which has the properties of a bisulphide. It sinters at 195° and melts at 208° ; on reduction with zinc and hydrochloric acid, the acetyl derivative is regenerated. The *diacetyl* derivative crystallises from alcohol in slender, yellow needles ; it sinters at 168° and melts at 176°. M. O. F.

**Thebaine.** By MARTIN FREUND and ERNST GÖBEL (*Ber.*, 1895, **28**, 941—944 ; compare this vol., i., 117).—When thebaine is heated during several hours with acetic anhydride, it yields methylhydroxyethylamine and the *acetyl* derivative of thebaol, which melts at 118—122° and is insoluble in alkalis. *Thebaol*,  $\text{C}_{11}\text{H}_7(\text{OMe})_2\text{OH}$ , is obtained from the acetyl derivative ; it melts at 94°. *Acetylthebaol* is also formed when thebaine methiodide is treated with boiling acetic anhydride in presence of silver acetate, dimethylhydroxyethylamine being produced at the same time ; on oxidation with chromic anhydride and glacial acetic acid, it yields *acetylthebaolquinone*, which crystallises in yellow needles and melts at 203°. *Thebaolquinone*,  $\text{C}_{11}\text{H}_5\text{O}_2(\text{OMe})_2\text{OH}$ , forms brown leaflets and melts at 233° ; it condenses with tolylenediamine forming the phenanthrazine derivative,  $\text{OH} \cdot \text{C}_{14}\text{H}_5(\text{OMe})_2 < \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Me}$ , which melts at 192°, whilst the *compound* derived from acetylthebaolquinone crystallises in yellow needles and melts at 201—203°.

These observations confirm the view already put forward regarding the constitution of thebaine (*loc. cit.*), which is derived from a



dihydrophenanthrene, whilst morphine and codeine, to which thebaïne is closely related, are tetrahydrophenanthrene derivatives.

M. O. F.

**Brucine Hydropolysulphide.** By OSCAR G. DOEBNER (*Arch. Pharm.*, 1994, **232**, 693—697).—When an alcoholic solution of brucine is treated with a solution of sulphur in alcoholic ammonium sulphide, a *hydropolysulphide*,  $(C_{23}H_{26}N_2O_4)_2H_2S_8 + 2H_2O$ , is formed. The orange-red crystals are insoluble in water, alcohol, ether, benzene, and carbon bisulphide. The hydropolysulphide retains the characteristic physiological properties of brucine, although in a lessened degree. This compound appears to be different from the brucine polysulphide obtained by E. Schmidt, which probably contained 6 atoms of sulphur, and was analogous to the strychnine hexasulphide first prepared by Hofmann.

L. T. T.

**Cinchotenine.** By FLORIAN RATZ (*Monatsh.*, 1894, **15**, 787—802; compare Skraup, *Annalen*, 197).—The *ethyl derivative* of cinchotenine,  $C_{18}H_{19}EtN_2O_3$ , obtained on treating the alkaloid with ethylic iodide and sodium ethoxide, melts at  $210.5^\circ$ , and gives the following derivatives:—A *hydrochloride*,  $C_{18}H_{19}EtN_2O_3 \cdot 2HCl$ , which decomposes at  $231$ — $232^\circ$ ; a *platinochloride*,  $C_{18}H_{19}EtN_2O_3 \cdot H_2PtCl_6$ , which decomposes at  $200^\circ$ ; an *ethiodide*,  $C_{18}H_{19}EtN_2O_3 \cdot EtI$ , crystallising in pale yellow needles, which melt and decompose at  $212$ — $213^\circ$ ; and a *sesquiethiodide*,  $[C_{18}H_{19}EtN_2O_3]_2 \cdot 3EtI$ , which crystallises in bright yellow needles, melts and decomposes at  $183^\circ$ , and when treated with hot water is converted into a mixture of the *monethiodide* described above and a *diethiodide*,  $C_{18}H_{19}EtN_2O_3 \cdot 2EtI + H_2O$ . The latter crystallises in deep yellow prisms, and melts at  $154^\circ$ . Ethylcinchotenine does not appear to change when treated with nitrous acid.

With acetic chloride, cinchotenine yields the compound



a pale yellow, crystalline powder, which is insoluble in ether and melts and decomposes at  $183$ — $184^\circ$ . With benzoic chloride, cinchotenine forms an amorphous, yellow powder,  $C_{18}H_{19}BzN_2O_3 \cdot HCl + H_2O$ , which melts and decomposes at  $197^\circ$ , and does not form an additive compound with hydriodic acid, so that the double linking existing in cinchonine appears to be broken through during the oxidation to cinchotenine.

G. T. M.

**Cinchotenine.** By PAUL FORTNER (*Monatsh.*, 1895, **16**, 62—67).—When cinchotenine and phosphorus pentachloride are mixed with phosphorus oxychloride, and heated for some hours at  $100^\circ$ , a product is obtained which is probably an acid chloride, since, on treatment with water and alcohol, it yields cinchotenine and ethylcinchotenine respectively. This behaviour, taken in conjunction with the facts that cinchotenine readily undergoes ethylation, and that it dissolves in cold, dilute alkaline solutions, points to the presence of a carboxyl group in the alkaloid.

G. T. M.

**Action of Hydriodic acid on Cinchotine and on Hydroquinine.** By GUSTAV PUM (*Monatsh.*, 1895, **16**, 68—74).—*Cinchotine*

*dihydriodide*,  $C_{19}H_{24}N_2O_2 \cdot 2HI$ , forms anhydrous, yellow crystals, which darken at  $232^\circ$ , and melt and decompose at  $263$ – $264^\circ$ . It remains unchanged when heated for five hours at  $100^\circ$  with hydriodic acid.

*Hydroquinine dihydriodide*,  $C_{20}H_{26}N_2O_2 \cdot 2HI$ , separates from a solution in 50 per cent. alcohol in bright yellow crystals containing  $3H_2O$ . On heating with hydriodic acid at  $100^\circ$ , the salt  $C_{19}H_{24}N_2O_2 \cdot 2HI$  is obtained. It forms yellow crystals, which turn brown at  $228^\circ$  and melt and decompose at  $239$ – $240^\circ$ . The corresponding base, obtained by the addition of sodium carbonate to the hydriodide, darkens at  $165^\circ$ , melts at  $170^\circ$ , and, unlike hydroquinine, is readily and perfectly soluble in aqueous potash. It is noteworthy that cinchotine and hydroquinine have not the same power to take up hydrogen iodide as is possessed by cinchonine and quinine, each of which contains 2 atoms of hydrogen less than the bases first named.

G. T. M.

**Cinchonigine.** By ÉMILE JUNGFLERSCH and EUGÈNE LÉGER (*Compt. rend.*, 1895, **120**, 325–328).—Cinchonigine (Abstr., 1888, 308, 507, 612) is dimorphous, and with the exception of strontium hydrogen tartrate, which does not exist in solution, it is the first example of a dimorphous compound with a specific rotatory power.

When a carefully dried ethereal solution of cinchonigine is allowed to crystallise at the ordinary temperature, the crystals are monoclinic, but, if crystallisation takes place in the hot solution, the crystals belong to the rhombic system. Different portions of the same solution will yield the two different kinds of crystals according to the temperature of crystallisation, and the tendency to form one or the other is increased by the introduction of ready-formed crystals. Further, if a monoclinic crystal is added to the rhombic crystals in ether at a low temperature, they are gradually and completely transformed into monoclinic crystals. On the other hand, if the monoclinic crystals, moistened with ether saturated with cinchonigine, are mixed with a rhombic crystal and heated in a sealed tube at  $45$ – $50^\circ$  for some hours, the whole mass changes to rhombic crystals. Both crystals melt at the same temperature, and when converted into the hydrochloride have the same rotatory power; their salts and other derivatives are also identical.

Cinchonigine, which when dry melts at  $129^\circ$ , melts in boiling water, and the liquid on cooling deposits crystals of a hydrate, which is best obtained by saturating ether with both water and cinchonigine and allowing it to evaporate slowly. The crystals are rhombic and hemihedral; they contain  $2H_2O$ , melt at  $69.3^\circ$  (corr.), and are stable in ordinary air, but lose their water in dry air or at  $100^\circ$ . The closely related cinchoniline forms a hydrate with  $3H_2O$ .

C. H. B.

## Organic Chemistry.

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**Action of Magnesium on the Vapours of the Alcohols.**  
**Preparation of Allylene.** By EDWARD H. KEISER and MARY B. BREED (*Chem. News*, 1895 **71**, 118—120).—Magnesium glows when heated in a current of the vapour of methylic, ethylic, or propylic alcohol; a large volume of gas is at the same time given off, and a black, coherent mass remains, which, on treatment with water and a small quantity of ammonium chloride, evolves a moderately rapid current of allylene. The gas evolved during the glowing of the magnesium had the following percentage composition.

	With methylic alcohol.	With ethylic alcohol.	With propylic alcohol.
CO <sub>2</sub> .....	0·8	0·0	0·0
CO.....	0·6	0·4	3·5
CH <sub>4</sub> or saturated hydro- carbons.....	19·7	11·1	19·9
C <sub>2</sub> H <sub>2</sub> } or unsaturated {	—	10·0	17·8
C <sub>2</sub> H <sub>4</sub> } hydrocarbons.. {	—	4·0	
H.....	78·9	72·9	57·8

The decomposition of the same alcohols by passing the vapour over heated iron, yielded gases of the following percentage composition.

	Methylic alcohol.	Ethylic alcohol.	Propylic alcohol.
CO <sub>2</sub> .....	3·8	0·5	0·6
CO.....	26·8	8·0	16·4
Saturated hydrocarbons	1·6	13·0	23·6
Unsaturated hydrocar- bons.....	—	4·0	16·7
Hydrogen.....	67·4	63·8	42·7

In the case of the magnesium, the carbonic oxide is reduced. Allylic, isobutylic, and amylic alcohols were found to behave in a similar manner; a small quantity of acetylide was found in the black residue in the case of propylic alcohol. The production of allylene from propylic and allylic alcohols, in the manner described, proceeds with such facility that it is recommended as a method of preparing allylene.  
D. A. L.

**Crystalline Copper-ferrocyanides.** By J. MESSNER (*Zeit. anorg. Chem.*, **8**, 368—393).—When potassium ferrous ferrocyanide, K<sub>2</sub>Fe(FeC<sub>6</sub>N<sub>6</sub>), is treated with ferric salts and water, a violet amorphous precipitate is obtained, containing from 6 to 12 per cent. of potassium, according to the temperature at which the action takes place. If a cupric salt is employed in place of the ferric salt, then a beautiful, violet compound is obtained, which, like the iron compound, is converted by oxidation into a green powder. This violet com-

pound, which probably has the composition  $K_2CuFe_2(FeC_6N_6)_2$ , is slowly and incompletely decomposed by boiling with alkali carbonates or hydroxides, and the solution so obtained contains copper, which can be precipitated by hydrogen sulphide. If the violet compound is decomposed by potassium carbonate, the solution, on cooling, deposits crystals of the compound obtained by boiling copper ferrocyanide with potassium ferrocyanide; this compound cannot, however, be obtained pure. When sodium carbonate is employed in place of potassium carbonate, the compound  $Na_2Cu(FeC_6N_6)$  is obtained in beautiful, brown, quadratic prisms.

*Sodium cuproferrocyanide*,  $Na_2Cu_2(FeC_6N_6)$ , is obtained by adding a cold saturated solution of the double cyanide of copper and sodium to a hot solution of sodium ferrocyanide. It crystallises from the solution, on cooling, in colourless, microcrystalline, six-sided prisms, and may be dried in a vacuum over sulphuric acid. It is also obtained by boiling a solution of sodium ferrocyanide with cuprous cyanide, and, after adding a small quantity of neutral sodium sulphite, cooling the solution in a current of hydrogen. The compound contains 27.5 per cent. of water. When exposed to the air, it slowly oxidises and turns brown. When heated at  $100^\circ$ , it turns brown and loses part of its water of crystallisation, but the whole of the water of crystallisation can only be removed by ignition. At  $200^\circ$ , it glows and decomposes, and at  $180^\circ$ , it is converted into a brown powder which still contains water. It is insoluble in water, alcohol, and ether, dissolves in alkali cyanides with decomposition, and is decomposed by acids and alkalis.

*Sodium cupriferrrocyanide*,  $Na_2Cu(FeC_6N_6)$ , is formed when cupric salts are boiled with a solution of sodium ferrocyanide. It is most easily prepared by boiling copper ferrocyanide, prepared from copper sulphate and hydroferrocyanic acid, with sodium ferrocyanide, and, after filtering off the amorphous precipitate, allowing the filtrate to evaporate exposed to the air. Or it can be obtained by passing a current of air through the hot mother liquors of the cuprous salt and then allowing the oxidised compound to crystallise. It crystallises in lustrous, brown, four-sided prisms, is insoluble in cold water, and decomposes when boiled with water or with dilute acids or alkalis. It dissolves in potassium cyanide with evolution of cyanogen, and yields potassium cuprous cyanide and potassium ferrocyanide. When copper ferrocyanide is boiled with a solution of sodium ferrocyanide, a bright green compound is produced, which is converted into the brown compound after one to two hours' boiling; this phenomenon does not take place in the case of the potassium salts. The author was unable to determine whether the green substance is a definite compound, as it is very easily decomposed. The mother liquors of sodium cupriferrrocyanide and sodium cuproferrocyanide, when mixed with dilute acids, yield white, amorphous precipitates, which are probably the acids  $H_2Cu(FeC_6N_6)$  and  $H_2Cu_2(FeC_6N_6)$ . When freshly prepared, they dissolve in alkali carbonates and hydroxides, and quickly decompose to yield ferrocyanic acid.

*Potassium cuproferrocyanide*,  $K_2Cu_2(FeC_6N_6)$ , is obtained in like manner to the sodium salt by boiling copper cyanide with a solution

of potassium ferrocyanide containing a small quantity of potassium sulphite, or by boiling potassium cuprous cyanide or cuprous chloride with potassium ferrocyanide. It crystallises in colourless cubes if the solution is quickly cooled. When the solution is slowly cooled, it is obtained mixed with partially oxidised crystals of a yellow to brown colour. It contains 18.7 to 20.4 per cent. of water, and closely resembles the sodium salt.

The author was unable to obtain potassium cupriferrrocyanide in a pure state, as under all conditions the cupro-salt is formed at the same time.

*Ammonium cuproferrocyanide* is obtained by boiling copper cyanide with a solution of ammonium ferrocyanide containing ammonium sulphite and passing hydrogen through the mixture. It crystallises in small, colourless, six-sided prisms, decomposes rapidly under water, or on exposure to air, or in a vacuum, with formation of hydroferrocyanic acid, and is at once decomposed by acids and alkalis. It can also be obtained by treating a solution of the sodium salt with ammonium nitrate.

*Ammonium cupriferrrocyanide* is obtained by boiling copper ferrocyanide with a solution of ammonium ferrocyanide. The solution thus obtained must be filtered as quickly and as hot as possible. It crystallises in brownish-red cubes, can be dried in a vacuum over sulphuric acid, and has properties similar to those of the sodium salt.

*Magnesium cuproferrocyanide* is obtained by boiling copper cyanide with a solution of magnesium ferrocyanide. It crystallises in beautiful, colourless, six-sided prisms, turns brown on exposure to air and in a vacuum over sulphuric acid, and is less stable than the analogous sodium and potassium salts.

*Magnesium cupriferrrocyanide* is easily obtained by boiling copper ferrocyanide with magnesium ferrocyanide. It separates in violet-brown crystals and contains 44.3 to 44.5 per cent. of water.

*Calcium cupriferrrocyanide* crystallises in small, brown, quadratic prisms, and can be dried in a vacuum over sulphuric acid.

*Strontium cupriferrrocyanide* and *barium cupriferrrocyanide* are obtained in crystals having the same form and colour as the calcium salt.

*Calcium, strontium, and barium cuproferrocyanides* are obtained by boiling copper cyanide with the corresponding ferrocyanides. They crystallise in colourless, six-sided prisms, which cannot be distinguished from one another, but the pure compounds cannot be obtained as the simple ferrocyanide always separates with them, and an excess of ferrocyanide is necessary in their preparation, as the cuproferrocyanides are not soluble in water except in the presence of an excess of ferrocyanide.

*Copper ferrocyanide ammonia*,  $\text{Cu}_2(\text{FeC}_6\text{N}_6) \cdot 8\text{NH}_3$ , is obtained by adding a solution of ammonium ferrocyanide in strong ammonia to a solution of cuprous chloride in the strongest ammonia, and allowing the mixture to remain for a few hours. It crystallises in beautiful, black, lustrous prisms, is very sparingly soluble in ammonia, and is not decomposed by cold absolute alcohol. The crystals, on exposure to air, quickly decompose into ammonia, copper ferrocyanide, and the compound  $\text{Cu}_2(\text{FeC}_6\text{N}_6) \cdot 4\text{NH}_3$ . With dilute acids, it yields copper

ferrocyanide and ammonium salts. When evaporated on the water bath in its own mother liquor, it is converted into ammonium cupri-ferrocyanide and amorphous compounds. E. C. R.

**A New Alcohol from Lanolin.** By G. MARCHETTI (*Gazzetta*, 1895, **25**, i, 42—49).—After hydrolysing lanolin by heating it on the water bath with alcoholic sodium ethoxide, distilling off the solvent, acidifying with sulphuric acid, and extracting the cholesterol, alcohols, and aliphatic acids with ether, a residue of *lanolinic alcohol*,  $C_{12}H_{24}O$ , remains; on purification with alcohol and chloroform, it is obtained as a white, odourless powder, or as spheroidal concretions, melting at  $102\text{--}104^\circ$ . It is soluble in hot alcohol, chloroform, or benzene, but insoluble in potash or ether; it is precipitated unchanged by acids from its solution in sodium ethoxide, and is not acted on by iodine or acetic anhydride. The *benzoate*,  $C_{12}H_{23}OBz$ , forms a white, waxy mass, melting at  $65\text{--}66^\circ$ , which decomposes on exposure to the air, and is hydrolysed by sodium ethoxide.

*Lanolinic acid*,  $C_{12}H_{22}O_3$ , is prepared by oxidising lanolinic alcohol with chromic acid in acetic acid solution; it is a white, crystalline powder, melting at  $75\text{--}77^\circ$ , and is soluble in alcohol, ether, chloroform, benzene, or alkali carbonates, but is insoluble in water. Its *barium salt*,  $(C_{12}H_{21}O_3)_2Ba$ , crystallises with  $1H_2O$  which is lost at  $150^\circ$ , and decomposes when heated. W. J. P.

**The Polymerides of Epichlorhydrin.** By EMANUELE PATERNÒ (*Gazzetta*, 1894, **24**, ii, 541—544).—The author supplements Oliveri and Paternò's cryoscopic examination of the polymeride of epichlorhydrin (*Abstr.*, 1894, i, 486) by new determinations in benzene and acetic acid, and by boiling point determinations in benzene; the results of these experiments indicate that the substance probably has the molecular composition  $(C_3H_5ClO)_5$ . The behaviour in freezing benzene shows that the compound has marked alcoholic properties; on treatment with cold alcoholic potash, it yields an oil, which boils at  $250\text{--}300^\circ$  with slight decomposition, and yields about 53 per cent. of ethoxyl by Zeisel's method; it possibly has the composition  $C_{12}H_{20}(OEt)_4O_4$ . W. J. P.

**Amorphous Condition of Fused Substances.** By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 630—632).—The glucose pentacetins (this vol., i, 321) crystallise in needles, whilst the hexacetins of racemo-inositol and the active inositols form hard and somewhat bulky crystals. If, however, they are melted in narrow tubes and allowed to cool, they all solidify in amorphous forms, which melt at  $40\text{--}50^\circ$  below the normal melting points. When the amorphous forms are melted, they gradually change into the crystalline forms with normal melting points, the change being more rapid the smaller the difference between the melting points of the crystallised and amorphous forms. The change from amorphous to crystalline is accompanied by development of heat, and is strictly analogous to the conversion of plastic sulphur into the crystalline form. It would follow that there is no essential difference between the allo-

tropic modifications of the element and the crystallised and amorphous forms of the compounds in question.

Many other carbon compounds behave like the acetins and solidify in an amorphous form when melted and suddenly cooled. When heated, however, the amorphous forms become crystalline with development of heat, the change being very rapid in some cases and gradual in others.

C. H. B.

**Combination of Sugars with Primary Hydrazines: Amidoguanidine, and Arabinose.** By R. RADENHAUSEN (*Chem. Centr.*, 1894, ii, 776; from *Zeit. Ver. Rübenzuck.-Ind.*, 1894, 768—770; compare H. Wolff, *Abstr.*, 1894, i, 315).—Amidoguanidine reacts with arabinose in alcoholic solution, a condensation with the aldehyde group occurring with separation of water; the product crystallises in small, white needles, melts at 125° (uncorr.), and dissolves in water and in alcohol, but not in ether.

The reaction between hydrazine hydrate and arabinose gives rise to a deep-seated decomposition of the sugar, and no crystalline product has been isolated. Nitrobenzoylhydrazine and arabinose, however, form a condensation product, which crystallises in snow-white tablets, and melts at 178°; it is insoluble in cold water, and is decomposed into the parent substances when heated with water—a behaviour which is remarkable, since all compounds of hydrazines with aldehydes which have been prepared heretofore are stable in hot water.

A. G. B.

**A Second Achroodextrin obtained by the Action of Diastase on Starch.** By CARL J. LINTNER and GEORG DÜLL (*Chem. Centr.*, 1894, ii, 864; *Zeit. ges. Brauw.*, 1894, 17, 339—340).—The new dextrin, hitherto overlooked because it forms only a small proportion of the products of conversion, has the formula  $(C_{12}H_{20}O_{10})_3 + H_2O$ . The opticity is  $[\alpha]_D = 183^\circ$ , and the cupric reduction  $R = 26.5$ — $26.8$ . No evidence of a third achroodextrin,  $(C_{12}H_{20}O_{10})_2 + H_2O$ , has been obtained. This new achroodextrin II has the same composition as that of the substance described by Brown and Morris as typical maltodextrin, but the opticity and cupric reduction given for this substance leave no doubt that it is not pure, but contains both achroodextrin I and isomaltose.

A. G. B.

**Wax Found in the Treatment of Cotton and Linen Fibre for the Manufacture of Paper.** By CLAYTON BEADLE (*Chem. News*, 1895, 71, 164—165).—Occasionally when disintegrating fibre that has been treated under pressure with  $3\frac{1}{2}$  per cent. caustic soda and bleached with calcium hypochlorite at 32°, a deposit forms on surfaces in the beater. This consists of aluminium, iron, and calcium salts mixed with a sweet-smelling waxy substance, soluble in ether, melting at 47.5°, having a saponification equivalent of 19.46 (KHO), and yielding 91.04 per cent. of insoluble fat acids. It is not noticed in the raw fibre.

D. A. L.

**Derivatives of Active  $\alpha$ -Hydroxybutyric acid.** By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1895, 120, 632—635).—

The ethereal salts of the lævogyrate  $\alpha$ -hydroxybutyric acid (this vol., i, 333) were prepared in the usual way; their physical properties are as follows, the alkylic radicles being primary in all cases.

	Boiling point.	Sp. gr. at 15°.	Specific rotatory power $[\alpha]_D$ .	Product of asymmetry $P \times 10^6$ .
Ethylic salt .....	169°	0.978	-1.9	319
Normal butylic salt..	200	0.982	-9.7	309
Isobutylic salt.....	197	0.965	-7.7	309
Racemic amylic salt..	209	0.950	-8.5	286
Heptylic salt.....	245	0.928	-6.1	233
Octylic „ .....	255	0.916	-5.3	209

The maximum of  $P$  corresponds with the propylic salt, the value being 330. The rotatory power also passes through a maximum, but the two maxima do not coincide.

The results obtained with the various amylic salts are as follows.

	$[\alpha]_D$ .
1. Racemic hydroxybutyric acid and active alcohol .....	+1.5
2. Lævogyrate hydroxybutyric acid and racemic alcohol.	-8.5
3. „ „ „ and lævogyrate alcohol.....	-7.3
4. Dextrogyrate „ „ and lævogyrate alcohol .....	+8.1

These results afford further proof of the superposition of the effects of different asymmetrical carbon atoms in the same molecule. The calculated rotatory power of ethereal salt No. 3 is -7.0, and the observed value -7.3; in the case of No. 4 the calculated and observed values are +7.8 and +8.1 respectively (compare this vol., ii, 149 and 195).  
C. H. B.

**Condensation of Ketones with Ethylic Salts of Dibasic Acids under the Influence of Sodium Ethoxide.** By HANS STOBBE (*Ber.*, 1895, 28, 1122-1123).—In consequence of the publications of Japp and Davidson (*Trans.*, 1895, 132) and Meyenberg (this vol., i, 334), the author states that he is extending his research (*Abstr.*, 1894, i, 594), and examining the condensation of various ketones and diketones with ethylic succinate, pyrotartrate and malonate, and of the last with ethylic acetoacetate. From acetone and ethylic malonate, two acids have already been obtained melting at 74-76° and at 146-148°.  
C. F. B.

**Condensation of Ethylic Malonate with Acetone.** By KARL AUWERS (*Ber.*, 1895, 1130-1133).—In an attempt to synthesise nor-camphoric acid, now given up on account of Meyenberg's paper (this vol., i, 334), ethylic dimethylacrylate,  $\text{CMe}_2\text{CH}\cdot\text{COOEt}$ , was condensed by heating it with ethylic potassiummalonate and a little alcohol at 98°, and a compound,  $\text{CH}(\text{COOEt})_2\text{CMe}_2\text{CH}\cdot\text{COOEt}$ , was obtained; the ethylic salt, after the potassium is replaced by hydrogen, boils at 194° under 43 mm. pressure, and has sp. gr. = 1.064 at



13.5°. When hydrolysed with rather strong acids, it yields  $\beta\beta$ -dimethylglutaric acid,  $\text{CMe}_2(\text{CH}_2\cdot\text{COOH})_2$ ; this melts at 100–101°, and, when treated with acetic chloride or distilled under atmospheric pressure, yields an anhydride melting at 124°.

$\beta$ -Bromisovaleric acid was prepared by treating dimethylacrylic acid with hydrobromic acid saturated at 0°; it melts at 73.5°.

C. F. B.

**Conversion of Carbamide into Cyanamide.** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1894, [3], 11, 1068–1070; compare Fenton, *Trans.*, 1882, 262).—Carbamide is readily and energetically dehydrated by sulphurous chloride, abundance of sulphurous anhydride and hydrogen chloride being evolved when the two are mixed. After the excess of the reagent has been removed by means of sodium carbonate solution, the cyanamide is extracted from the product with ether.

JN. W.

**Mercuric Compound of Thiophen: Estimation of Thiophen in Benzene.** By GEORGES DENIGÈS (*Compt. rend.*, 1895, 120, 628–630).—The compounds of mercury with thiophen hitherto known are formed from the chloride under special conditions, but the author finds that thiophen combines readily with mercuric sulphate in acid solution, and also with mercuric acetate and chloride under similar conditions. The reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. If 200 c.c. of this liquid is mixed with 1 c.c. of thiophen, it rapidly becomes turbid at the ordinary temperature, but the liquid should be first gently heated, and finally boiled.

A basic mercuriothiophen sulphate,  $(\text{HgSO}_4\cdot\text{HgO})_2\text{C}_4\text{SH}_4 + \text{H}_2\text{O}$ , separates as a heavy, coherent, white, precipitate, formed of radiating spherulids, and is washed with boiling water and dried. It loses 1 mol.  $\text{H}_2\text{O}$  at 100–110°, and may be heated for a long time at 120–130°, or even at 150°, without undergoing any further change. Above 200°, sulphurous anhydride and thiophen are given off. It is insoluble in water and neutral solvents, but dissolves in acids, with gradual liberation of thiophen, as indicated by the isatin and alloxan or alloxantin reactions, the change being accelerated by heat. Hydrogen sulphide or alkali sulphides precipitate the mercury and liberate thiophen, but ammonia and caustic alkalis have no action even on heating.

The ease with which this compound is formed, and its insolubility, affords a valuable means of detecting and estimating thiophen in commercial benzene.

C. H. B.

**Hexamethylene.** By NICOLAI D. ZELINSKY (*Ber.*, 1895, 28, 1022–1025).—Hexamethylene, prepared by reducing iodo-hexamethylene (Baeyer, *Abstr.*, 1894, i, 174) in alcoholic solution with zinc and hydrochloric acid, boils at 81–82°, has the sp. gr. 0.7764 at 20°/4°, and the refractive index 1.4258. Hexahydrobenzene, prepared by the direct reduction of benzene with hydriodic acid (Kishner, *J. Russ. Chem. Soc.*, 1894, 375), on the other hand, boils at 72–73°, has the sp. gr. 0.7488, and the refractive index 1.4101, so that the two com-

pounds seem to be distinct. The hydrocarbon, prepared by the reduction of iodoexamethylene with hydriodic acid at  $220^{\circ}$ , has properties which are intermediate between those of the two substances just described, and probably contains both of them.

A. H.

**The Use of Metallic Aluminium in the Synthesis of Aromatic Hydrocarbons.** By CORNELIUS RADZIEWANOWSKI (*Ber.*, 1895, 28, 1135—1140).—Instead of aluminium chloride, aluminium itself, together with either hydrochloric acid or mercuric chloride, may be used to effect the Friedel-Crafts synthesis. A small quantity of aluminium shavings is placed in excess of benzene, gaseous hydrogen chloride passed in for 20 minutes, and the mixture allowed to remain until the metal turns brown and a copious evolution of hydrogen begins; the chloride or bromide of the other radicle is then added drop by drop, the mixture being cooled with water, or the chloride or bromide is added drop by drop to a mixture of aluminium shavings and mercuric chloride with excess of benzene, the mixture being cooled with ice. Diphenylmethane and ethylbenzene were prepared by both methods from benzylic chloride and ethylic bromide respectively; isopropylbenzene, from isopropyl chloride, by the first method only. This method does not bring about the condensation with chloroform to triphenylmethane, nor with benzylic chloride to anthracene. The second method will effect the first of these condensations, but not the second. The yield was usually 60—70 per cent. of the theoretical.

C. F. B.

**Argon in Combination.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 581—584).—When argon is mixed with benzene vapour and subjected repeatedly to the action of the silent electrical discharge, the benzene being renewed from time to time, condensation takes place and a product is formed similar to that obtained from benzene and nitrogen under similar conditions; it is a yellow resinous odorous substance which when heated yields alkaline vapours and an abundant carbonaceous residue.

If the molecular weight of argon were 42, it would stand in this respect in the same relation to nitrogen as ozone does to oxygen.

C. H. B.

**Ethylquinone.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1130—1131).—*Ethylquinone*, prepared from dimethylanilethylquinonimide (this vol., i, 417), crystallises in brilliant, golden-yellow plates, or long, prismatic needles. It has a powerful odour, and its vapour irritates the eyes and nose. It melts at  $38.2^{\circ}$ , and is readily volatile at ordinary temperatures. The corresponding *quinol*,



prepared by reducing the quinone with sodium hydrogen sulphite, crystallises in colourless plates or prismatic needles, and melts at  $112$ — $113^{\circ}$ ; it sublimes easily. The solution in alkalis soon becomes coloured.

JN. W.

**Purification of Guaiacol by strongly Cooling it.** By LUDWIG WENGHÖFFER (*Chem. Centr.*, 1894, ii, 565; from *Pharm. Zeit.*, 1894, 39, 576—577).—Liquid guaiacol is kept for a day at a temperature of  $-100^{\circ}$  and then separated, by a peculiar artifice, into two layers; the larger and clearer of these is "Riedel-Pictet guaiacol," the other is a brownish-yellow residue. Riedel's guaiacol has a sp. gr. at  $24^{\circ}$  of 1.1099, and dissolves to the extent of 1 part in 88 parts of water; the Riedel-Pictet guaiacol has sp. gr. = 1.1171 at  $24^{\circ}$ , and dissolves in 80 parts of water; the residue from the above treatment has sp. gr. = 1.0889 at  $24^{\circ}$ , and dissolves in 200 parts of water. The three products yield 46 grams, 49 grams, and 8 grams of acetyl-guaiacol per 50 grams, respectively, when acetylated. Guaiacol purified in this manner does not become coloured when exposed to light, and is only feebly coloured by strong sulphuric acid.

A. G. B.

**Aromatic Selenium Compounds.** By P. CAMILLE CHABRIÉ (*Bull. Soc. Chim.*, 1894, [3], 11, 1080—1083).—A criticism of Krafft and his collaborators (*Abstr.*, 1894, i, 88, 448). The author has prepared various aromatic selenium compounds by synthesis with aluminium chloride. Phenyllic hydroselenide is completely soluble in alcohol, and forms definite crystals melting at  $60^{\circ}$ ; the analytical results, moreover, are in good agreement with those calculated from the formula  $\text{PhSeH}$ ; it cannot, therefore, be a mixture of phenyllic selenide and diselenide with selenium, as stated by Krafft. It is true that the analytical results agree equally well with those required by diphenylic diselenide, but it is not likely to be the latter, as it forms compounds with mercury analogous to the mercaptides. Diphenylic diselenoxide is an oily liquid boiling at  $230^{\circ}$  (65 mm.), and not a crystalline solid, as stated by Krafft; neither does it decompose into phenyllic selenide when distilled. The dibromide melts at  $120^{\circ}$ . *Chlorodiphenylic selenoxide*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SePhO}$ , occurs as a bye-product in the aluminium chloride process; it crystallises well, and melts at  $94^{\circ}$ .

JN. W.

**Manufacture of Orthonitraniline.** By JOSEPH POKORNÝ (*Chem. Centr.*, 1894, ii, 556; from *Bull. Soc. Indust. Mulhouse*, 1894, 280—284).—Forty grams (?) of acetanilide is gradually added to 80 kilos. of sulphuric acid ( $66^{\circ}\text{B}$ ), while the liquid is well stirred and the temperature not allowed to rise above  $50^{\circ}$ ; a mixture of 36 kilos. of nitric acid ( $36\text{--}37^{\circ}\text{B}$ ) with 40 kilos. of sulphuric acid ( $66^{\circ}\text{B}$ ) is allowed to flow into this solution of acetanilide, which is kept at a temperature of  $40\text{--}50^{\circ}$ , the application of cold and agitation being continued until the temperature of the liquid falls continuously. On the following day, the liquid is poured into 200 litres of hot water, whereon a yellowish precipitate, consisting of ortho- and par-nitracetanilide is thrown down. To deacetylate the mixture, it is heated by steam until all the precipitate is dissolved; the liquor is then cooled to  $50^{\circ}$  and poured into 200 kilos. of ice which is kept well stirred. Orthonitraniline is thus precipitated, whilst par-nitraniline may be thrown down from the mother liquor by mixing

it with 180 kilos. of soda-lye (36° B) and cooling with ice. The yield is 25 per cent. of ortho- and 60 per cent. of para-nitraniline.

A. G. B.

**Action of Phthalic Chloride on Nitranilines.** By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 1118—1120).—The results differ somewhat, especially as regards the melting points, from those of Dobreff (this vol., i, 360). With excess of phthalic chloride, nitrophthalanils,  $C_6H_4 \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} > N \cdot C_6H_4 \cdot NO_2$ , are obtained; with excess of the nitraniline, nitrophthalanilides,  $C_6H_4(CO \cdot NH \cdot C_6H_4 \cdot NO_2)_2$ ; the numbers given are melting points.

*Nitrophthalanils*; 1:4, white, amorphous, 262—263°; 1:3, white, amorphous or crystalline, 242—244°; 1:2, yellowish needles, 200—203°. *Nitrophthalanilides*; 1:4, yellowish powder, 232—234°; 1:2, silky yellowish needles, 180—184°; 1:3 (?), 232—234°.

C. F. B.

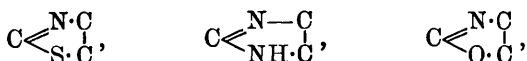
**Derivatives of Benzylamine.** By PAUL FRIEDLÄNDER and M. MOSCZYC (*Ber.*, 1895, **28**, 1140—1145).—1:4-Dimethylamidobenzylamine,  $NMe_2 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$ , is obtained by heating 1:4-nitrobenzyl chloride with dimethylamine in alcoholic solution, and reducing the product with stannous chloride; it is a colourless syrupy liquid, and boils with slight decomposition at above 300°; its *sulphate*, with  $H_2SO_4$ , crystallises in lustrous, yellowish plates. The corresponding *diethyl* compound boils at 212—214° under 40 mm. pressure. The methyl compound can be diazotised, and then yields with  $\beta$ -naphthol a basic azo-dye which crystallises in red needles and melts at 120°. It can also be converted by the diazo-reaction into the cyanide, the *platinochloride* of which was prepared.

If 1:4-toluenitrile is chlorinated at the boiling temperature, and the product treated with concentrated sulphuric acid, *w*-chloro-1:4-toluamide is formed, and by warming this with aqueous dimethylamine, *w*-dimethylamine-1:4-toluamide is obtained; this melts at 144°. Dilute alkalis convert it into the *acid*,  $NMe_2 \cdot CH_2 \cdot C_6H_4 \cdot COOH$ , melting at 235°, the *platinochloride* of which melts at 220—224°; when reduced with sodium amalgam, the acid yields dimethylamine and paratoluic acid. *w*-Chlorotoluic acid reacts with *w*-dimethylamine-paratoluic acid, yielding *dimethylamidodibenzylparadicarboxylic acid*,  $COOH \cdot C_6H_4 \cdot CH_2 \cdot CH(NMe_2) \cdot C_6H_4 \cdot COOH$ , which melts at 268—270°; the *hydrochloride* and *picrate* melt at 227° and 212° respectively. *w*-Chloroparatoluamide is converted by sodium ethoxide into an *ethoxy-compound* which melts at 112°, and is hydrolysed by soda to *w*-ethoxyparatoluic acid,  $OEt \cdot CH_2 \cdot C_6H_4 \cdot COOH$ , melting at 87°.

Paratoluic acid is converted by phosphorus pentachloride into the chloride, and when this is chlorinated at the boiling temperature, and that fraction of the product which boils at 265—270° treated with dimethylamine, *w*-dimethylamidoparatoluic acid is obtained. The aniline derivatives prepared were  $NHPh \cdot CH_2 \cdot C_6H_4 \cdot CO \cdot NHPh$ , m. p. 183°;  $NHPh \cdot CH_2 \cdot C_6H_4 \cdot CONH_2$ , m. p. 150°;  $NHPh \cdot CH_2 \cdot C_6H_4 \cdot COOH$ , m. p. 50°.

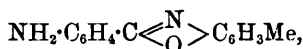
C. F. B.

**Amido-derivatives of Benzenylamidophenols.** By EUGEN LELLMANN and LUDWIG EBEL (*Ber.*, 1895, **28**, 1127—1129).—It has been already shown (*Abstr.*, 1894, i, 79) that substances containing the second of the groups—



like those containing the first, are substantive colouring matters; it is now shown that compounds containing the third of these groups are also substantive dyes.

1 : 4- and 1 : 3-*Amidobenzenyl*-1 : 2-*amido*-1 : 4-*cresols*,



were obtained by reducing with stannous chloride the corresponding nitrotylic salts of nitrobenzoic acids, themselves prepared by the action of 1 : 4- and 1 : 3-nitrobenzoic chlorides on nitrocresol [ $\text{Me} : \text{NO}_2 : \text{OH} = 1 : 3 : 4$ ]. The 1 : 4-base crystallises in two different forms, which melt at  $187^\circ$  and  $188^\circ$ ; the colourless 1 : 3-base melts at  $143$ — $144^\circ$ . Both bases yield red substantive dyes when diazotised, and combine with  $\beta$ -naphthol, &c. C. F. B.

**The Carbodiphenylimides.** By WILHELM V. MILLER and JOSEF PLÖCHL (*Ber.*, 1895, **28**, 1004—1012).—Schall has described (*Abstr.*, 1892, 1452) three isomeric carbodiphenylimides, the  $\alpha$ - and  $\beta$ -compounds being, according to him, stereoisomerides, whilst the  $\beta$ - and  $\gamma$ -compounds are physical isomerides. The authors have repeated his experiments, and find that there are only two distinct substances, the empirical formulæ of which are the same, but that the  $\beta$ -modification has three times the molecular weight of the  $\alpha$ -form, its molecular weight having been determined by the cryoscopic method in benzene solution. The  $\gamma$ -form appears to be simply a mixture of varying amounts of the  $\alpha$ - and  $\beta$ -compounds. A. H.

**Phenylimidocarbonates.** By ARTHUR HANTZSCH and LUDWIG MAI (*Ber.*, 1895, **28**, 977—984).—Phenylimidocarbonates,  $\text{NPh} \cdot \text{C}(\text{OR})_2$ , are obtained by adding isocyanophenylchloride,  $\text{NPh} \cdot \text{CCl}_2$ , (1 mol.) to a solution of a substituted sodium phenoxide (2 mols.) in ether and alcohol, and heating the mixture at  $100^\circ$ ; when heated with strong hydrochloric acid, they yield aniline and carbonates,  $\text{CO}(\text{OR})_2$ . If only 1 mol. of sodium phenoxide is used, phenylimidochloroformates,  $\text{NPh} \cdot \text{CCl} \cdot \text{OR}$ , are obtained; when heated with alcohol, these yield phenylamidocarbonates (urethanes),  $\text{NHPh} \cdot \text{COOR}$ ; and when heated with sodium derivatives of phenols, mixed phenylimidocarbonates,  $\text{NPh} \cdot \text{C}(\text{OR}') \cdot \text{OR}$  are formed. These last could not be shown to exist in geometrically isomeric forms, an identical product,  $\text{NPh} \cdot \text{C}(\text{OPh}) \cdot \text{OC}_6\text{H}_4\text{Br}$ , being obtained either by the action of  $\text{NaO} \cdot \text{C}_6\text{H}_4\text{Br}$  on  $\text{NPh} \cdot \text{CCl} \cdot \text{OPh}$ , or of  $\text{NaOPh}$  on  $\text{NPh} \cdot \text{CCl} \cdot \text{OC}_6\text{H}_4\text{Br}$ . By these reactions the following substances were prepared; the numbers are melting points.

*Phenylic phenylimidocarbonate*,  $136^\circ$ . 1 : 4-*Bromophenylic phenyl*-

imidocarbonate,  $106^{\circ}$ ; di-1 : 4-bromophenylic carbonate,  $171^{\circ}$ . Phenyllic phenylimidochloro-formate,  $42-45^{\circ}$ ; boils at  $180^{\circ}$  under 15 mm., at  $199-200^{\circ}$  under 22 mm. pressure. 1 : 4-Bromophenylic phenylimidochloro-formate,  $45^{\circ}$ ; boils at  $227^{\circ}$  under 23 mm., at  $223^{\circ}$  under 22 mm. pressure; 1 : 4-bromophenylic phenylamidocarbonate,  $144^{\circ}$ ; 1 : 4-chlorophenylic phenylamidocarbonate,  $138^{\circ}$ . Phenyllic 1 : 4-bromophenylic phenylimidocarbonate,  $83^{\circ}$ .

Isocyanophenylchloride reacts with piperidine in ethereal solution as it does with aniline, and yields phenyldipiperidylguanidine,  $\text{NPh}\cdot\text{C}(\text{NC}_5\text{H}_{10})_2$ , melting at  $84^{\circ}$ . The phenylimidochloro-formates (see above) also react with piperidine and with ammonia, yielding "isocarbamides,"  $\text{NPh}\cdot\text{C}(\text{NHR}')\cdot\text{OR}$ . Of these, phenyl-1 : 4-bromophenylisocarbamide,  $142^{\circ}$ , was prepared with ammonia; diphenylpiperidylisocarbamide,  $86^{\circ}$ , and phenyl-1 : 4-bromophenylpiperidylisocarbamide,  $91^{\circ}$ , with piperidine.

C. F. B.

**Preparation of Paraquinones from Indophenols.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1129—1130).—Indophenol,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , and its homologues are hydrolysed by acids into dimethylparaphenylenediamine and quinone or homologues of the compound. The substance is merely dissolved in moderately strong sulphuric acid (7 parts of 40 per cent. acid), and the cooled solution extracted with ether. The product obtained on removing that solvent is then distilled with steam and recrystallised from a mixture of alcohol and ether. With the indoparaxylols, indocarvacrol, and indothymol, the yield of the quinone is quantitative, but with indophenol and the indocresols somewhat less, the stability of the molecule appearing to decrease as the number of groups attached to the benzene nucleus increases.

JN. W.

**Indophenols.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1131—1136).—The author has prepared several indophenols by the process used in the preparation of indothymol (Abstr., 1892, 1311), namely, by oxidising mixtures of dimethylparaphenylenediamine and the respective phenols with potassium dichromate in acetic acid solution, the diamine hydrochloride being prepared at the time by reducing paranitrosodimethylaniline hydrochloride with zinc dust. The yield is usually good.

The indophenols appear to crystallise in the triclinic system. They are practically insoluble in water, although the latter is coloured an intense blue by the trace dissolved, but they dissolve freely in the usual organic solvents yielding violet or blue solutions. As stated in the preceding abstract, they are hydrolysed by mineral acids into dimethylparaphenylenediamine and the respective quinones.

Dimethylanilquinonimide (indophenol),  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ , crystallises in steel-gray needles, and darkens at  $100^{\circ}$ , owing to the loss of its water of crystallisation; the anhydrous salt melts at  $133-134^{\circ}$ . Dimethylanilorthotoluquinonimide crystallises in rhombic needles, green by reflected light, and melts at  $123^{\circ}$ . The corresponding meta-compound crystallises in prisms, golden-yellow by reflected light, and melts at  $117-118^{\circ}$ . Dimethylanilparaxyloquinonimide,

$\text{O}:\text{C}_6\text{H}_2\text{Me}_2:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$  ( $\text{O}:\text{Me}_2:\text{N} = 1:2:5:4$ ), crystallises in reddish-brown plates and melts at  $125-126^\circ$ . *Dimethylanilethylquinonimide*,  $\text{O}:\text{C}_6\text{H}_3\text{Et}:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$  ( $\text{O}:\text{Et}:\text{N} = 1:2:4$ ), crystallises in long, rhombic plates, golden-yellow by reflected light, and melts at  $83-84^\circ$ . *Dimethylanilthymoquinonimide*,  $\text{O}:\text{C}_6\text{H}_2\text{MePr}:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$  ( $\text{O}:\text{Me}:\text{Pr}:\text{N} = 1:3:4:6$ ), crystallises in triclinic, rhomboidal plates, also golden-yellow by reflected light, and melts at  $87-88^\circ$ .

JN. W.

**Reduction of Aromatic Nitro-derivatives in Neutral Solution: Formation of Aromatic Hydroxylamines.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWITZ (*Bull. Soc. Chim.*, 1894, [3], 11, 1038—1045; compare Bamberger, *Abstr.*, 1894, i, 373, 412, and Wohl, *ibid.*, 409, 450).—Wohl and Bamberger's method of reducing nitro-compounds to  $\beta$ -hydroxylamines by means of zinc dust and water is not applicable to the nitrophenols and nitranilines, as these substances are completely reduced to the corresponding amidophenols and diamines by that reagent. The method, however, promises to be of commercial importance for the preparation of the latter bases, as the yield is extremely good, and the products pure. Ortho- and para-amidophenol and ortho- and para-phenylenediamine can be prepared in this way, and certain dinitro-compounds, such as dinitrobenzene, dinitronaphthalene, and 1:2:4-dinitrophenol, appear to undergo a similar reduction.

The homologues of nitrobenzene, on the other hand, readily yield substituted hydroxylamines, provided a small quantity of calcium or other chloride be present.  $\beta$ -*Paratolylhydroxylamine*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{OH}$ , crystallises from benzene in well-developed plates and melts at  $92-93^\circ$ . It is easily oxidised to paramethylazoxybenzene, azoxy-paratoluene, or amidocresol, and is, of course, a powerful reducing agent. The *hydrochloride* crystallises in colourless needles. The *nitroso-derivative*,  $\text{NO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{OH}$ , forms colourless crystals and melts at  $57-58^\circ$ . *Additive compounds* with benzaldehyde and formaldehyde were also prepared; the benzaldehyde compound is crystalline and melts at  $120^\circ$ . Paratolylhydroxylamine may be used as a developer in photography.  $\beta$ -*Orthotolylhydroxylamine* is an oil having properties similar to those of the para-compound.  $\beta$ -*Pararylhydroxylamine*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NHOH}$  ( $\text{Me}_2:\text{NHOH} = 1:4:5$ ), forms colourless crystals and melts at  $88-89^\circ$ . The *hydrochloride* crystallises in colourless plates.  $\alpha$ -Nitronaphthalene yielded a liquid product having strong reducing properties, but nothing could be isolated from it but  $\alpha$ -naphthylamine.

JN. W.

**Action of Hydroxylamine on Phthalic Anhydride.** By GIORGIO ERRERA (*Gazzetta*, 1894, 24, ii, 469—474).—*Hydroxylamine phthalylhydroxamate*,  $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{NH}_2\cdot\text{OH}$ , is prepared by mixing alcoholic solutions of hydroxylamine hydrochloride and sodium ethoxide, separating the deposited sodium chloride and adding phthalic anhydride to the solution; the salt separates as a colourless, crystalline substance soluble in water; its solutions give a red coloration with ferric chloride, and reduce Fehling's solution. It decomposes at  $130-135^\circ$ , yielding phthalylhydroxylamine, hydroxyl-

amine, and water; ammonium phthalylhydroxamate is also formed as a product of secondary action.

By employing a smaller proportion of hydroxylamine than that used in the above preparation, sodium phthalylhydroxamate is obtained.  
W. J. P.

**Isomerism in the Azo-series.** By ARTHUR HANTZSCH (*Ber.*, 1895, **28**, 1124—1126).—The compounds obtained by Bamberger (this vol., i. 351) from nitrodiazobenzene salts and  $\alpha$ -naphthol are not, as he thinks, stereochemically isomeric, but are structurally isomeric, the  $\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  group occupying, in the  $\alpha$ - and  $\beta$ -compound respectively (melting at 277—279° and 235°), the 4- and 2-positions with respect to the OH of the naphthol. This is shown by the fact that the two compounds, when reduced with stannous chloride, yield respectively 4 : 1- and 2 : 1-amidonaphthol.  
C. F. B.

**Methylphenyldithiobiuret and Methylphenylthiuret.** By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1096—1101; compare *Abstr.*, 1893, i, 575).—*Methylphenyldithiobiuret* (*biuramine*) was prepared by heating methylaniline with perthiocyanic acid,  $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$ , at 100°; it forms white crystals, melts at 156°, and dissolves in alkalis, but not in dilute acids. When it is oxidised with iodine, it reacts as if it had the constitution  $\text{NMePh}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{C}(\text{SH})\cdot\text{NH}$ , and yields *methylphenylthiuret*,  $\text{NMePh}\cdot\text{C}\leq\text{N}^{\text{S}_2}>\text{C}\cdot\text{NH}$ . This substance could not be isolated, but it acts as a monacid base, and its *hydrochloride*, *hydrobromide*, and yellow *hydriodide* melt respectively at 232°, 220°, and 193°; when boiled with aqueous potash, it yields ammonia and methylaniline.  
C. F. B.

**Condensation of Methylphenyldithiobiuret with Aldehydes and Ketones.** By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1102—1113).—When methylphenyldithiobiuret (compare preceding abstract) is mixed with an aldehyde or ketone,  $\text{O}\cdot\text{CXR}$ , and hydrogen chloride passed into the mixture, it reacts as if it had the constitution  $\text{NMePh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , and yields compounds  $\text{NMePh}\cdot\text{CS}\cdot\text{N}\leq\text{CXR}^{\text{CS}}>\text{NH}$ . With acetone, it yields  $\alpha$ -methylphenyl-dithio-dimethylketuret, melting at 152°; with benzaldehyde,  $\alpha$ -methylphenyldithiophenylalduret, melting at 168°; with acetaldehyde, the reaction is anomalous. When the above-mentioned keturet and alduret are dissolved in cold alcoholic soda, and the solutions allowed to remain with benzylic chloride, *monobenzyl derivatives* are formed, melting respectively at 85° and 127°. When these are heated on the water bath with strong hydrochloric acid, they are decomposed; the keturet yields, besides methylaniline, ammonia, carbonic anhydride, hydrogen sulphide, benzylic hydrosulphide, and bisulphide, some acetone and benzylic imidotrithiodicarboxylate,



doubtless formed by the action of benzylic hydrosulphide on the compound  $\text{CSOH}\cdot\text{NH}\cdot\text{COSC}_7\text{H}_7$  first formed. In the case of the



alduret, the last compound is not formed; benzaldehyde is liberated in place of acetone, and benzylic hydrosulphide reacting more readily with it than it does with acetone, the compound  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{SC}_2\text{H}_5)_2$  is obtained, and no benzylic imidotrithiodicarboxylate. This substance is however obtained, together with the compound mentioned, if excess of benzylic hydrosulphide is present from the beginning of the reaction. *Benzylic imidotrithiodicarboxylate* crystallises in yellowish needles, and melts at  $144-145^\circ$ ; when treated with alcoholic ammonia, it yields monothiobiuret.

C. F. B.

**Combination of Benzaldehyde with Hydrocyanic acid in Dilute Solution.** By E. UTSCHER (*Chem. Centr.*, 1894, ii, 675—676; from *Pharm. Post*, 27, 417—421).—Contrary to Glücksmann the author maintains that the combination of benzaldehyde with hydrogen cyanide is a very rapid process even in dilute solution. Benzaldehyde was mixed with hydrocyanic acid and alcohol in the proportion of 1 part of the acid to 6 parts of the aldehyde, the solution containing 0.1 per cent. of hydrogen cyanide in one experiment and 0.2 per cent. in another. In the case of the 0.2 per cent. solution, 0.0845 per cent. of acid was left uncombined after 60 hours, 0.0245 per cent. after five days, and 0.0137 per cent. after 10 days. In water with 0.1 per cent. of hydrogen cyanide, the combination is more gradual. The author has already shown that benzaldehyde cyanhydrin is not completely decomposed by dilute potash. Hydrogen cyanide which has been mixed with excess of ammonia, then with excess of nitric acid, and with N/10 silver nitrate solution, shows when titrated by Volhard's method a lower content of hydrogen cyanide the longer the time which is allowed to elapse between the addition of the nitric acid and of the silver nitrate; thus, in a quarter of an hour the amount indicated dropped from 0.503 per cent. to 0.495 per cent. Glücksmann used a hydrocyanic acid solution of about half this strength; he also employed too small a proportion of benzaldehyde.

A. G. B.

**Condensation of Mandelic acid with Phenols.** By AUGUSTIN BISTRZYCKI and J. FLATAU (*Ber.*, 1895, 28, 989—991).—When mandelic acid (5 parts) is heated with phenol (7 parts) in the presence of 73 per cent. sulphuric acid (20 parts), a compound is formed which is probably *hydroxydiphenylacetic lactone*,  $\text{CHPh}<\overset{\text{C}_6\text{H}_5}{\underset{\text{CO}}{\text{C}}}>\text{O}$ ; the yield is 22 per cent. of the theoretical. The lactone melts at  $113-114^\circ$ , and boils at  $337^\circ$ ; when boiled with aqueous, sodium carbonate, it yields the sodium salt of the acid, which itself melts at  $85-87^\circ$ . In a similar manner *phenyl-1:4-cresylacetic acid* and its lactone were obtained from mandelic acid and 1:4-cresol; they melt at  $118^\circ$  and  $106^\circ$  respectively.

C. F. B.

**Coumarincarboxylates and a New Synthesis of Coumarin.** By PIETRO BIGINELLI (*Gazzetta*, 1894, 24, ii, 491—503).—*Ethyllic methahydroxycoumarin- $\beta$ -carboxylate*,  $\text{C}(\text{OH})\cdot\text{CH}\cdot\text{C}\cdot\text{C}(\text{COOEt})\cdot\text{CH}$   
 $\text{CH}=\text{CH}\cdot\text{CO}\text{-----}\text{CO}$ , is

obtained by adding concentrated sulphuric acid to a solution of quinol in ethylic oxalacetate; it exists in two modifications which are separated by crystallisation from alcohol and ether; the least soluble modification crystallises in yellow laminæ melting at 177—178°, whilst the more soluble crystallises in yellow prisms melting at 180—182°. The former isomeride may be converted into the modification of higher melting point by boiling with dilute alcohol, and the author concludes that they are stereoisomerides. The ethylic salts are accompanied by small quantities of the free *acids* which are, however, best prepared by hydrolysing these salts with potash, adding acid, and crystallising from water; the one acid crystallises in thin, yellow needles melting at 279—280°, whilst the other forms acicular laminæ melting at 283—284°. When heated at 280—290°, the acids distil with partial decomposition, and are deposited in yellow laminæ melting at 289°. The *sodium* salt crystallises from water in needles containing  $1\text{H}_2\text{O}$ , which is lost at 100°, but is deposited from alcohol in prisms containing  $\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{EtOH}$ ; the salt is very soluble in water, and, on treatment with acids, yields the acid melting at 280°.

Although carbonic anhydride is evolved on heating the above acid, the hydroxycoumarin cannot be isolated from the residue, and can only be prepared from the acid by the process described below.

*Methylic metamethoxycoumarin-β-carboxylate*,  $\text{OMe}\cdot\text{C}_9\text{H}_4\text{O}_2\cdot\text{COOMe}$ , is obtained by treating the above acid in methylic alcoholic potash solution with methylic iodide; it crystallises in needles, melts at 131—132°, and is readily hydrolysed by alkalis yielding the corresponding *acid*, which crystallises in yellow laminæ melting at 246—247°. On heating the acid with iron dust, or its sodium salt with caustic soda, the metamethoxycoumarin melting at 102—103° is obtained; on treatment with hydriodic acid, it yields the meta-hydroxycoumarin melting at 249°. W. J. P.

**Triacetylgallic acid.** By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1894, [3], 11, 937).—A reply to Schiff (this vol., i, 368).

**Triacetylgallic acid.** By PAUL SISLEY (*Bull. Soc. Chim.*, 1894, [3], 11, 938—939).—Boettinger's triacetylgallic acid (*Abstr.*, 1884, 1178) is identical with the author's diacetylgallic acid (this vol., i, 283). Boettinger's pentacetyltannin (*loc. cit.*) is identical with the triacetylgallic acid of Schiff and the author (*loc. cit.*).

As diacetylgallic acid does not give a colour reaction with ferric chloride, the absence of a coloration with that reagent must not be taken as conclusive evidence of the absence of phenolic hydroxyl from the molecule. JN. W.

**Hemipinic acid and its Ethereal Salts.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1895, 16, 75—152; compare *Abstr.*, 1882, 1206, and 1891, 712).—Hemipinic acid,  $\text{C}_6\text{H}_2(\text{OMe})_2(\text{COOH})_2 = [1 : 2 : 3 : 4]$ , is most readily obtained by treating opianic acid oxime with potash, or by oxidising opianic acid itself with potassium permanganate. This acid appears to exist in only one modification; the different melting points, varying from 160° to 178°, given by different authori-

ties, are due to the fact that it is partially converted into the anhydride even before it melts. The amount of anhydride thus formed depends on the length of time during which the acid is heated, and consequently the melting point also varies with the rate of heating.

The monalkylic salts of hemipinic acid form two isomeric series, the  $\alpha$  and  $\beta$ , the normal alkylic salts only one.

	Methylic.	Ethylic.	Normal propylic.
Normal salt, m. p. =	61—62°	72°	43—45°
$\alpha$ -acid salt, m. p. =	121—122	144.0—145°	119.0—120.0° and 131—132.0°
$\beta$ -acid salt, m. p. =	137—138	147.5—149	111.5—112.5 and 125—125.5

The  $\alpha$ -monethylic and both  $\alpha$ - and  $\beta$ -monopropylic hemipinate occur in desmotropic forms. The two  $\alpha$ -ethylic salts have the same melting point, but differ in other physical properties. The propylic salts have the melting points given above.

All the monalkylic salts when heated yield hemipinic anhydride and the corresponding alcohol.

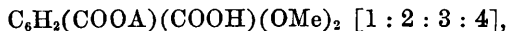
The  $\alpha$ -ethereal salts are best obtained—(1) By the oxidation of the true ethereal salts of opianic acid. (2) By boiling hemipinic anhydride with the requisite alcohol; a small quantity of the  $\beta$ -salt is also formed in this reaction. (3) By heating potassium hydrogen hemipinate with alcohols and alkylic iodides; this reaction is, however, incomplete. (4) By the hydrolysis of the normal ethereal salts.

The  $\alpha$ -ethereal salts give a yellow coloration and milky turbidity with very dilute ferric chloride solution.

The isomeric  $\beta$ -derivatives are best obtained by saturating a solution of the acid in alcohol with dry hydrogen chloride. The  $\beta$ -salts are the first products formed, but if the saturation is carried out for several hours at the boiling point of the alcoholic solution, normal salts are also obtained, and these, in the presence of the hydrogen chloride, become hydrolysed to the  $\alpha$ -salts.

The silver salts of both  $\alpha$ - and  $\beta$ -derivatives, when heated at 200—230° under a pressure of 21 mm., are decomposed, and yield ethylic veratrate, together with hemipinic acid.

The  $\alpha$ -salts have the constitution  $C_6H_2(COOH)(COOA)(OMe)_2$  [1 : 2 : 3 : 4], since they are obtained by the oxidation of the corresponding opianates; and the constitution



for the  $\beta$ -series follows from the law of V. Meyer and Sudborough. The author discusses the theories of Friedel and of Henry, regarding the etherification of acids, by means of alcohol and hydrogen chloride, in the light of the recent observations of Meyer and Sudborough. Henry's hypothesis, according to which the etherification is preceded by the addition of the elements of the alcohol to the carbonyl group of the acid, is considered the more probable. It may be, however, that it is the hydrogen chloride and not the alcohol which unites with the carbonyl group. The presence of substituting groups in the ortho-positions may thus prevent the formation of such additive compounds, just as according to Meyer and Sudborough's theory such

groups can prevent the direct entry of alkyl radicles. If this is true, then we must expect to meet similar phenomena in the formation of imido-ethers, amidines, and amidoximes. Similarly diortho-substituted aldehydes should be incapable of taking part in reactions which require the formation of additive compounds.\* Hemipinic and camphoric acids exhibit very similar phenomena when etherified, but as the constitution of camphoric acid has not been definitely determined, the two series cannot be very closely compared. It can be shown, however, that the etherification does not depend on the strength of the carboxylic group, as in hemipinic acid the weaker carboxylic group is the first to be etherified, but in camphoric acid the reverse is true. By the action of alkalis on the normal ethereal salts of both acids, the first carboxylic group to be hydrolysed is the one which is the first to be etherified.

J. J. S.

**Preparation of Ethylenediphenylsulphone.** By ROBERT OTTO and K. MÜHLE (*Ber.*, 1895, **28**, 1120—1122).—*Ethylenediphenylsulphone* (Escales and Baumann, *Abstr.*, 1887, 123) can be conveniently prepared by oxidising ethylenedithiophenyl, prepared from ethylenic dichloride and sodium thiophenoxide (*J. pr. Chem.*, [2], **51**, 518), with permanganate in acetic acid solution, and removing the admixed manganese oxide with sulphurous anhydride.

C. F. B.

**Derivatives of Benzylideneacetophenone.** By CARL GOLDSCHMIDT (*Ber.*, 1895, **28**, 986).—Benzylideneacetophenone yields two *oximes*, melting respectively at 68° and 140°; the latter is gradually transformed into the former when kept. It also yields two *nitro-derivatives*; one melts at 159°, the other is an oily 1 : 2-derivative, which yields 2'-phenylquinoline when reduced with stannous chloride.

C. F. B.

**Paratoluoylorthobenzoic acid and Benzophenonedicarboxylic acid.** By HEINRICH LIMPRICHT (*Ber.*, 1895, **28**, 1134—1135).—Paratoluoylorthobenzoic acid could not be obtained crystallised with H<sub>2</sub>O, as Friedel and Crafts describe it; the melting point, further, was 138—139° instead of 146°. When oxidised with permanganate, it yields *benzophenonedicarboxylic acid*, CO(C<sub>6</sub>H<sub>4</sub>·COOH)<sub>2</sub>, which crystallises with H<sub>2</sub>O and also anhydrous; the anhydrous acid melts at 239°, its *methylic salt* at 107°. With acetic anhydride, the acid yields a *diacetyl derivative*, melting at 182°. The *acid chloride* melts at 110°, and, when treated with zinc-ethyl in ethereal solution, yields the *ketone*, CO(C<sub>6</sub>H<sub>4</sub>·CO·C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, which melts at 105°.

C. F. B.

**A Colour Reaction of Carbazole.** By GIACOMO CARRARA (*Gazzetta*, 1894, **24**, ii, 535—540).—On heating carbazole (1 mol.) with salicylaldehyde (2 mols.) and concentrated sulphuric acid at 100—110°, an intensely blue product is obtained; it contains, in addi-

\* V. Meyer (*Ber.*, 1895, **28**, 1267) has shown that this is probably true for Perkin's reaction.—J. J. S.

tion to carbazolemono- and di-sulphonic acids, an amorphous reddish colouring matter, which forms a barium salt, contains much sulphur, and is soluble in water, alcohol, ether, and benzene. It dyes mordanted silk and cotton, and is still under investigation.

W. J. P.

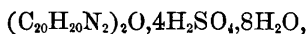
**New Series of Colouring Matters.** By CHARLES FRIEDEL (*Bull. Soc. Chim.*, 1894, [3], 11, 1027—1028).—*Dimethyldiazidomethyl-*

*diphenylchloromethane hydrochloride*, 
$$\text{N} \begin{array}{c} \text{CMe} \text{---} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{CMeCl} \cdot \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CH} \text{---} \text{CMe} \end{array} \text{N} \cdot \text{HCl},$$

formed by the action of phosphoric oxychloride on methylacetanilide at 120°, is probably a condensation product of methylacetanilide with its acetyl derivative, as hydrogen chloride and methylaniline are eliminated in the reaction. It crystallises from alcohol, in which it dissolves to a crimson solution, in small needles, which are blue by reflected and red by transmitted light. As the *dihydrochloride* is practically colourless, the base promises to be of use as an indicator in alkalimetry, for the acid solution is coloured crimson even by aniline; the colour is discharged, however, by carbonic anhydride and acetylacetone, although it is not affected by phenol. The hydrochloride dyes wool and silk as well as cotton mordanted with tannin, but the colour, although unaffected by soap, is not very fast to light, and is of course discharged by acids.

When the hydrochloride is boiled with alkali sulphites, it is converted into the *sulphite*  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{SO}_3$ , a substance crystallising in small, golden, rhomboidal plates having a greenish metallic lustre; this is insoluble in water, but soluble in hot alcohol, yielding a violet solution, and is decomposed by hydrochloric acid. The *benzoate* crystallises in small needles having a greenish, metallic lustre. The *nitrate* and *acetate* are also coloured.

When a stream of air is passed through the boiling hydrochloric acid solution of the sulphite, the latter is converted into *dimethyldiazidomethyl-diphenylmethylic oxide*,  $(\text{C}_{20}\text{H}_{20}\text{N}_2)_2\text{O} \cdot \text{H}_2\text{O}$ , which is precipitated in crimson flakes by caustic alkalis, and crystallises from alcohol in orange prisms. The *sulphate* of this oxide,



crystallises in colourless, rectangular plates, and is rose-coloured when anhydrous. The oxide is reconverted into the original chlorinated base by the action of phosphoric oxychloride in benzene solution, but by the prolonged action of this reagent is transformed into a *blue colouring matter*, which is also formed from the original hydrochloride by oxidation with air in presence of alkali.

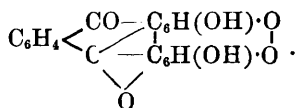
On distilling the hydrochloride with zinc dust, a *leuco-base*,  $\text{C}_{20}\text{H}_{22}\text{N}_2$  or  $\text{C}_{20}\text{H}_{24}\text{N}_2$ , is obtained as a colourless oil, boiling at about 260°. The *platinochloride* of this base was prepared. JN. W.

**Coloured Sulphonic Derivatives of Triphenylmethane.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], 11, 1188—1190).—Solutions of "acid rosaniline,"  $\text{OH} \cdot \text{C}[\text{C}_6\text{H}_3(\text{SO}_3\text{Na}) \cdot \text{NH}_2]_3$ , and other sulphonated colouring matters of the same type, are decolourised by

caustic alkalis, but quickly regain their colour on the addition of ammonium chloride. Rosenstiehl's view that the free substance is alcoholic and colourless does not offer any explanation of these facts, and is, in fact, in direct contradiction to them. If, however, it be granted that the free substance is acidic and coloured, whilst its sodium salt is colourless, an explanation is at once forthcoming. The ammonium salt, like the sodium salt, will be colourless, but prone to dissociation, so that, when the ammonium chloride is added, a considerable amount of the free acid will be liberated, and the colour restored. If this assumption be true, a solution of the dye, which has been decolorised by excess of ammonia, should tend to regain its colour on heating, but lose it again on cooling, unless the ammonia has been expelled by the heat, and this is actually the case. A further confirmation is found in the behaviour of an alkaline solution to which an equivalent amount of ammonium chloride has been added; on evaporating the solution to dryness, the residue, which can contain nothing but sodium chloride and the free hydroxylic substance, or its anhydride, regains the colour of the dye.

JN. W.

**Cœruleïn.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], 11, 1136—1138).—When cœruleïn is fused with aniline hydrochloride, a blue colouring matter is formed, which dyes bluish-green with iron and chromium mordants, and blue with those of aluminium. The condensation can be effected with the base itself by heating with a slight excess until the product appears to be dry, 2 mols. of aniline entering into combination, and 2 mols. of water being eliminated. The condensation product, after removal of the excess of aniline at 180°, is a violet powder, brownish-red by reflected light. It is sparingly soluble in water, but easily in concentrated sulphuric acid to a solution, which is blue when diluted, and from which the base is precipitated in greenish flocks by alkalis. The acetate dyes mordanted cotton greenish-blue, and wool and silk blue without mordants, but the colours are not fast to soap, owing to the liberation of the greenish base by the alkali. The base does not combine with the mordants of the aluminium group, so that its molecule does not contain hydroxyl. Since 2 mols. of water are eliminated in the condensation, it is probable that the cœruleïn molecule contains two hydroxyl groups; and as it also contains a phenylanthranol nucleus, its constitution may possibly be represented by the formula



JN. W.

**1 : 4-Dimethylnaphthol.** By STANISLAO CANNIZZARO and AMERICO ANDREOCCHI (*Gazzetta*, 1895, 25, i, 53—59).—The oxidation product of the dimethylnaphthol obtained by the decomposition of santanous acid (*Abstr.*, 1894, i, 143), is probably an oxydimethylnaphthol of the constitution  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{C} - \text{CMe} \cdot \text{CO} \end{array}$ ; it yields a crystalline oxime which

melts at  $175^{\circ}$ , and a *monhydrazone*, crystallising in long, red needles melting at  $83-84^{\circ}$ , and, on reduction, yields the original dimethylnaphthol. On treatment with hydrochloric acid, the oxime yields a green crystalline *anhydride*, which is converted into a stable and volatile *isomeride* by alcoholic potash; this substance crystallises in red needles and melts at  $173^{\circ}$ .

An *acetyldimethylnaphthylamine*,  $C_{10}H_5Me_2NHAc$  [= 1 : 4 : 2], is obtained by heating the dimethylnaphthol with acetamide under pressure; it crystallises in small, colourless prisms melting at  $218-220^{\circ}$ . On hydrolysis with sodium ethoxide at  $150^{\circ}$ , it yields the corresponding *dimethylnaphthylamine*, which crystallises in colourless prisms melting at  $74^{\circ}$ , boils at  $333^{\circ}$  under 745 mm. pressure, and gives the above acetyl derivative with acetic anhydride. On oxidation with permanganate, the amine yields an *azodimethylnaphthalene*, which crystallises in small, red needles melting at  $253^{\circ}$ ; it is accompanied by a colourless, crystalline *acid*, still under examination.

W. J. P.

**Phenolnaphthaleïn.** By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 991—994).—Although phenol and naphthalic anhydride do not condense when heated together in the presence of most dehydrating agents, they do so when aluminium chloride is the agent used. The product, *phenolnaphthaleïn*,  $CO < \overset{O^-}{C_{10}H_6} > C(C_6H_4 \cdot OH)_2$  [ $CO : C = 1 : 1'$ ], is a white substance, and melts and decomposes at  $120^{\circ}$  when amorphous, and at  $200^{\circ}$  when crystalline; its solution in alkalis has a red colour, with rather more of a bluish shade than is the case with phenolphthaleïn. With phosphorus pentachloride, it yields a *chloride*,  $C_{24}H_{14}O_2Cl_2$ , melting at  $180^{\circ}$ ; with hydroxylamine, a yellowish *oxime* melting at  $220^{\circ}$ .

C. F. B.

**Action of Carbamide on Quinones.** By SIRO GRIMALDI (*Gazzetta*, 1895, **25**, i, 78—79).—Phenanthraquinone and carbamide readily interact, giving two crystalline compounds, the one of which,  $C_{15}H_{10}N_2O_2$ , melts at  $299^{\circ}$ , whilst the other,  $C_{16}H_{12}N_4O_2$ , does not melt at  $320^{\circ}$ , and yields a crystalline *dinitro-derivative*,  $C_{16}H_{10}N_4O_2(NO_2)_2$ . With thiocarbamide and ammonium thiocyanate, phenanthraquinone yields a *dithioureide*,  $C_{16}H_{12}N_4S_2$ .  $\beta$ -Naphthaquinone reacts with carbamide, forming a *monoureide*,  $C_{11}H_8N_2O_2$ ; anthraquinone similarly yields a *monoureide*,  $C_{15}H_{10}N_2O_2$ , whilst quinone gives a crystalline *monoureide*,  $C_7H_6N_2O_3$ , which does not melt at  $320^{\circ}$ .

W. J. P.

**Essence of Cananga.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1894, [3], **11**, 1045—1051).—Cananga oil from Java has a sp. gr. = 0.9058 at  $21^{\circ}$ , a refractive index,  $\mu = 1.49655$ , and a specific rotatory power,  $[\alpha]_D = -28.5^{\circ}$ . The proximate constituents appear, on the whole, to be the same as those of essence of Ylang-ylang (this vol., i, 294), but their relative amounts are different. Thus, on hydrolysis, the cananga essence also yields acetic and benzoic acids, but only in small proportion, whilst a relatively large amount of volatile oil is obtained; this, again, contains but a small quantity of the alcoholic substance, the major portion consisting of a sesquiterpene.

The *sesquiterpene* boils at 252—257°; the sp. gr. = 0.9024 at 17°; the specific rotatory power,  $[\alpha]_D = -32.2^\circ$  at 20°; the refractive index,  $n = 1.50187$  at 17°. The molecular refraction = 66.8, and the iodine number = 255, so that two ethylene linkings are present in the molecule. The specific rotatory power, like that of other sesquiterpenes, is diminished, or even reversed, by heating at temperatures above 250°.

The *alcohol*,  $C_{10}H_{18}O$ , boils at 98—102° (20—21 mm.); the molecular refraction = 48.81, so that two ethylene linkings are present in the molecule, a conclusion confirmed by the iodine absorption.

Amongst the other substances isolated was an *oil* boiling at 166—173°, which, on oxidation with chromic acid mixture, yielded an acid,  $C_9H_{10}O_3$ , probably anisic acid.

Heine and Co., in a communication to the author, state that in addition to ylangol, they have isolated from essence of Ylang-ylang either geraniol, or some isomeride of that substance. J. N. W.

**Action of Nitrous acid on Oximes of the Camphor (Camphane) Series.** By ANGELO ANGELI and E. RIMINI (*Ber.*, 1895, 28, 1077—1078).—Camphoroxime, in glacial acetic acid solution, reacts with sodium nitrite; the product,  $C_{10}H_{16}N_2O_2$ , is crystalline, and melts at 43°. Camphenoxime yields a similar compound,  $C_{10}H_{14}N_2O_2$ , which melts at 47°. Both substances are insoluble in acids and alkalis, and neither of them gives Liebermann's reaction. Menthoneoxime appears to react with sodium nitrite in a similar manner (compare following abstract). J. B. T.

**Conversion of Camphor into an Isomeric Unsaturated Compound.** By ANGELO ANGELI (*Ber.*, 1895, 28, 1127).—The compound  $C_{10}H_{16}N_2O_2$ , obtained (preceding abstract) by the action of nitrous acid on camphoroxime, is attacked by cold strong sulphuric acid, a gas being evolved and a compound,  $C_{10}H_{16}O$ , isomeric with camphor, formed. This is an oily liquid, and yields an *oxime* melting at 106°. Both ketone and oxime immediately decolorise permanganate, and are therefore unsaturated compounds. C. F. B.

**Camphor.** By FERDINAND TIEMANN (*Ber.*, 1895, 28, 1079—1093).—*Camphorimine nitrate*,  $C_{10}H_{16}NH.HNO_3$ , is formed by the action of nitrous acid on camphoroxime; it is crystalline, and melts at 156°. *Camphorimine* is also crystalline, melts above 90°, evolves ammonia, and yields a number of decomposition products when exposed to air; it readily forms salts with acids, most of which are crystalline, and from them camphor may be regenerated. By the action of methylic iodide, *methylcamphorimine hydriodide*,  $C_{10}H_{16}NMe.HI$ , is formed.

*Camphenylnitramine*,  $C_8H_{14} < \begin{smallmatrix} CH \\ | \\ C-NH \cdot NO_2 \end{smallmatrix}$ , is formed, along with the imine; with alcoholic potash, it readily yields a crystalline *potassium* salt, which explodes violently on heating, and yields camphoric acid when oxidised with potassium permanganate. Determinations of its refractive power show that it contains a double linking (com-



pare preceding abstracts). By the action of hydriodic acid, camphor is formed; with ammonia, camphorimine is regenerated. The reaction has been studied in the case of other ketones and aldehydes; these differ both in the yield and also in the manner in which their oximes react with nitrous acid, but the method may be employed with advantage to convert isonitrosocamphor into camphorquinone.

Camphoroxime is readily converted into campholenitrile by the action of dehydrating agents (sulphuric acid, hydriodic acid), and this easily yields the amide by fusion with potash; when boiled with potash, it gives the amide and acid successively. The oxime and amide are lævogyrate, the nitrile and acid, like the original camphor, dextrogyrate. When the  $\alpha$ -nitrile is hydrolysed with acids and the product treated with alkali, *isamidocamphor*,  $C_{10}H_{15}O \cdot NH_2$ , is formed; it is a saturated primary base, extremely stable towards alkalis, readily changed by acids, has an unpleasant odour, is crystalline, melts at  $39^\circ$ , and boils at  $254$ — $256^\circ$  under normal pressure, and at  $152^\circ$  under 65 mm. pressure. The *salts* crystallise readily, and, when their solutions are heated,  $\beta$ -campholenamide,  $C_{10}H_{17}NO$ , is precipitated; this is also formed by the action of ammonia on  $\beta$ -campholenic acid (m. p.  $52^\circ$ ), it melts at  $86^\circ$ , regenerates the acid by treatment with potash, and has been recently described by Béhal (this vol., i, 241); he appears to have prepared it from a mixture of the  $\alpha$ - and  $\beta$ -nitriles; of these, the latter is more readily hydrolysed by potash than the former; his nitrile, regenerated from the hydrogen iodide derivative, yields a mixture of  $\alpha$ - and  $\beta$ -amide (m. p.  $92^\circ$ ).  $\alpha$ -Campholenitrile is readily prepared by heating camphoroxime with sulphuric acid (20 per cent.); it boils at  $225^\circ$ .  $\beta$ -Campholenitrile is best obtained by the prolonged heating of camphoroxime with dilute hydriodic acid; it boils at  $217^\circ$ . No optically active  $\beta$ -campholene derivatives have been prepared.

*Hydroxydihydrocamphenolactone*,  $C_{10}H_{16}O_2$ , is formed when isamidocamphor hydrochloride is allowed to remain for some time in aqueous solution at the ordinary temperature; it is also obtained by heating  $\alpha$ - or  $\beta$ -campholenic acid with strong acids; it boils and undergoes partial decomposition at  $255^\circ$ , is insoluble in water and soda at ordinary temperatures, and is not changed by boiling with water and calcium carbonate or, in ethereal solution, by treatment with ammonia. A *bromine derivative* is formed by the interaction of  $\beta$ -campholenic acid and bromine.

*Hydroxydihydrocampholenic acid*,  $C_{10}H_{16}O_3$ , crystallises in lustrous, colourless needles, melts at  $105^\circ$ , and is stable when pure, but traces of foreign substances cause its rapid conversion into the lactone. When quickly hydrolysed with alcoholic potash, the lactone is frequently converted into campholene, but the pure acid and  $\alpha$ - and  $\beta$ -campholenic acids are very stable towards alkalis; statements to the contrary made by various observers are due to the use of acids containing a little lactone; the varying descriptions given of  $\alpha$ - and  $\beta$ -campholenic acids is due to the same cause, since a trace of mineral acid suffices to convert  $\alpha$ -campholenic acid into the lactone, and the latter always yields some  $\beta$ -campholenic acid when distilled. Attention is drawn to the considerable alterations in boiling and melting

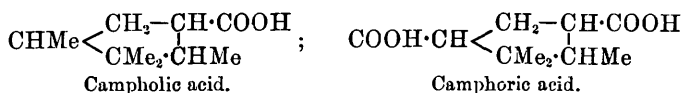
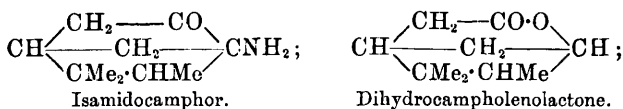
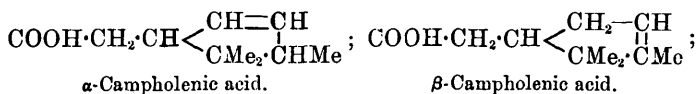
point produced in campholene derivatives caused by the presence of traces of impurity.

In discussing the constitution of camphor, exception is taken to Bredt's formula on the ground that it does not satisfactorily explain the behaviour of camphoroxime as a syn-derivative; if Bredt's formula is correct, the oxime should contain the complex  $\text{CMe} \cdot \text{C} \cdot \text{CH}_2$   $\begin{smallmatrix} \text{N} \\ \parallel \\ \text{O} \cdot \text{H} \end{smallmatrix}$  and campholenic acid, campholic acid, and camphoric acid should have the formulæ  $\text{CH}_2 \cdot \text{C}_8\text{H}_{13} \cdot \text{COOH}$ ,  $\text{C}_8\text{H}_{14}\text{Me} \cdot \text{COOH}$ , and  $\text{C}_8\text{H}_{14}(\text{COOH})_2$  respectively, they ought, therefore, to yield similar decomposition products, and campholenic acid should be readily converted into the other

acids. To overcome this objection, the formula  $\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH}$  is suggested for camphor; its conversion into cymene is preceded by the formation of a dihydrocarvone,  $\text{CHPr}^s \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} \text{CMe}$ . The

corresponding formula for fenchone,  $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe} - \text{CO} \end{smallmatrix} \text{CH}$ , obtains support from Wallach's work (*Annalen*, 1895, 284, 341).

For camphene and pinene, the formulæ  $\text{CH} \begin{smallmatrix} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH}$  and  $\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{C}$  respectively are deduced; the latter is in complete accord with investigations by the author and F. W. Semmler, which will be published shortly. The formulæ of the more important compounds referred to above are as follows.



In a supplementary note, Béhal's later communication (this vol., i, 241) is summarised and discussed. Béhal regards the campholenic acids as stereoisomeric, although unable to prepare an optically active form of the  $\beta$ -acid; the author points out that, although according to the above formula it contains an asymmetric carbon atom, the optical activity is lost as soon as a compound of the  $\alpha$ -series is converted into the  $\beta$ -series, even though haloid acids are excluded; he considers

that this supports his formula, and shows that the optical activity is dependent on the asymmetry or otherwise of the carbon atom in the CMe group.  
J. B. T.

**Derivatives of Quercetin.** By CARL T. LIEBERMANN (*Monatsh.*, 1895, 16, 180—182).—A reply to J. Herzig's criticisms on some of the author's previous analyses (*Abstr.*, 1884, 1365). It is shown that these old analyses agree very well with the new formula,  $C_{15}H_{10}O_7$ , suggested for quercetin by Herzig.  
J. J. S.

**Action of Potassium Permanganate and of Hydriodic acid and Red Phosphorus on Rottlerin.** By PIETRO BAROLOTTI (*Gazzetta*, 1894, 24, ii, 480—484; compare *Abstr.*, 1894, i, 301).—Rottlerin is readily oxidised by alkaline permanganate in the cold with formation of benzoic and oxalic acids; chromic acid attacks rottlerin very slowly, and only very little benzoic acid is formed.

Resinous products are obtained on heating rottlerin with hydriodic acid in sealed tubes at 210—220°, but, on heating at the same temperature with hydriodic acid and red phosphorus, a pleasant-smelling oil, lighter than water, is formed; it boils at 140—240°, and the fractions boiling at 140—150° and at 230—240° have the same composition, namely  $C_{10}H_{16}$  or  $C_{11}H_{18}$ . The examination of this oil is being continued.  
W. J. P.

**Yeast Glucose.** By CARL J. LINTNER and E. KRÖBER (*Ber.*, 1895, 28, 1050—1056).—Dried yeast, when extracted with water at ordinary temperatures, yields an enzyme which readily hydrolyses maltose; the temperature of maximum action is about 40°, and it is therefore different from invertin and from maize glucose, which act most readily at 52—53° and 57—60° respectively. The enzyme becomes inactive at 55°. Up to 35°, its action is proportional to the temperature, the quantity present, and the time of action remaining constant. Increase in the quantity of enzyme does not proportionately accelerate the inversion; the addition of chloroform considerably retards the hydrolysis, only about 70 per cent. of maltose being decomposed after 24 hours. The enzyme is without action on dextrin. Full analytical details are given, and the results are tabulated and illustrated by curves.  
J. B. T.

**Protochlorophyll.** By NICOLAI A. MONTEVERDE (*Ann. Agron.*, 1895, 21, 90; from *Acta horti. Petropolit.*, 1894, 201—217).—Etiolated leaves contain, besides xanthophyll and carotene, a colouring matter termed "protochlorophyll," which shows a red fluorescence; its absorption spectrum has a band corresponding with the chlorophyll band III, and another band at some distance from the chlorophyll band II, whilst the band I of chlorophyll is entirely wanting. The spectrum is displaced a little towards the right by alkalis. The substance in alcoholic solution is transformed by a few drops of hydrochloric or nitric acid into "protochlorophyllane." Protochlorophyll is separated as follows. The leaves are cut up, extracted with boiling water, pressed, and put into alcohol of 95°. The alcoholic solution

is precipitated with baryta, and the precipitate treated with alcoholic potash (10 per cent.). The alkaline solution of protochlorophyll thus obtained is straw coloured, with a feeble, red fluorescence.

When the alcoholic extract from etiolated wheat was exposed to sunlight, the chlorophyll band I appeared in three seconds, and the protochlorophyll spectrum gradually disappeared.

The spectrum, which Pringsheim and Tschirch considered to be characteristic of etioline, is a mixture of the spectra of slightly modified chlorophyll, protochlorophyll, carotene, and xanthophyll.

N. H. J. M.

**Action of Inorganic Chlorides on Piperidine and the Fatty Amines.** By C. A. AUGUST MICHAELIS (*Ber.*, 1895, 28, 1012—1019).

—*Thiopiperidine*,  $(C_5NH_{10})_2S$ , is obtained by the action of sulphur chloride,  $SCl_2$ , on piperidine; it crystallises in long prisms, which melt at  $74^\circ$ , and have a characteristic odour. It is not attacked by dilute alkalis, but dissolves in dilute acids, forming a clear solution, which soon decomposes, sulphur being deposited and sulphurous anhydride evolved. The *platinochloride* is a chocolate-brown precipitate, and the *picrate* melts at  $144$ — $145^\circ$ . *1-Thionylpiperidine*,  $(C_5NH_{10})_2SO$ , is obtained by the action of thionyl chloride on piperidine; it crystallises in white plates, and melts at  $46^\circ$ . It dissolves in acids, but very rapidly decomposes. When exposed to the air, thionylpiperidine is converted into a substance,  $C_5H_{11}NSO_2$ , which melts at  $70^\circ$  and deliquesces on further exposure to the air. It can also be obtained by passing a current of sulphurous anhydride into a solution of piperidine in dry ether. *Thiodiethylamine* is an almost colourless liquid, which boils at  $84$ — $86^\circ$  (15 mm. pressure), and resembles monothiopiperidine in its other properties. *Thionyldiethylamine* is a light yellow oil, which boils at  $118^\circ$  (27—28 mm. pressure), and also resembles the corresponding piperidine derivative.

*Tripiperidinephosphinozide*,  $(C_5H_{10}N)_3PO$ , is obtained by the action of phosphorus oxychloride on piperidine, and forms large plates which melt at  $75$ — $76^\circ$ . It dissolves in strong hydrochloric acid, and is not decomposed when this solution is heated. It does not form either a nitroso-derivative or an acetyl derivative. The *hydrochloride* crystallises in slender needles, and the *platinochloride* melts at  $215^\circ$ .

A. H.

**Derivatives of 4'-Phenylquinaldine and 4'-Phenylquinoline.**

By WILHELM KOENIGS and FRANZ MEIMBERG (*Ber.*, 1895, 28, 1038—1046).—The *sulphate* of phenylquinoline crystallises in nacreous tablets melting at  $195$ — $196^\circ$ ; the *hydrochloride* melts at  $96$ — $97^\circ$ , and forms double chlorides with many metallic chlorides; the *picrate* melts at  $224^\circ$ . The *methiodide* crystallises in long, compact, yellow needles, which melt at  $222^\circ$ . The *platinochloride* of the *methochloride* melts and decomposes at  $253^\circ$ . The methochloride is converted, by treatment with a cold solution of potassium ferricyanide, into

1': 4'-methylphenylquinolone,  $C_6H_4 < \begin{smallmatrix} CPh:CH \\ NMe \cdot CO \end{smallmatrix}$ , which separates from ether in serrated crystals melting at  $143$ — $144^\circ$ . When a solution of 4'-phenylquinoline in fuming sulphuric acid is allowed to stand, two

isomeric *monosulphonic acids* appear to be formed, both of which contain the sulphonic acid group in the 4'-phenyl residue. 4'-*Phenyltetrahydroquinoline* is produced by the action of tin and alcoholic hydrochloric acid on phenylquinoline, and crystallises in white, lustrous plates melting at 74°. The *hydrochloride* melts at 193—194°, the *sulphate* at 158°; the *platinochloride* decomposes and melts at 215°. The *acetyl* derivative crystallises in white plates and melts at 120°, and the *benzoyl compound* forms white needles melting at 147°. *Methylphenyltetrahydroquinoline* is an oil, which yields a *picrate* melting at 222—224°. The *nitrosamine* of phenyltetrahydroquinoline crystallises in flat, yellow needles, melts at 72°, and gives Liebermann's reaction. When treated with alcoholic hydrochloric acid, it is converted into the isomeric 4'-*phenylparanitrosotetrahydroquinoline*, which crystallises in small, green plates, and melts and decomposes at 199·5°. This compound is converted by reduction into 4'-phenylparamidoquinoline, which crystallises from chloroform in flat, faintly-coloured needles melting at 205°. Its ethereal solution has an intense blue fluorescence. The *picrate* melts at 233—234°, and the *platinochloride* forms orange-yellow needles.

The *hydrochloride* of 4'-phenylquinaldine crystallises in long, silky needles melting at 218—220°, and forms double chlorides with many metallic chlorides. The *picrate* crystallises in flat, yellow needles, and melts at 205—206°. The *methiodide* forms broad, yellow needles decomposing and melting at 205°; the *platinochloride* of the *methochloride* melts and decomposes at 245°. 4'-*Phenyltetrahydroquinaldine* crystallises in large, yellow-coloured tablets melting at 66—67°, whilst the *hydrochloride* melts at 221°. The *nitrosamine* forms small, yellowish needles melting at 97—98°.

With the object of obtaining 4'-phenylparahydroxyquinoline synthetically, the *paranisidide* of *benzoylacetone* was prepared by heating benzoylacetone with paranisidine. It crystallises in yellow needles, and melts at 107—108°. When heated with dilute or concentrated sulphuric acid, this compound is decomposed into its constituents, and does not yield the desired quinoline derivative. A. H.

**3-Methoxy-4'-phenylquinaldine: New Synthesis of  $\gamma$ -Phenylquinaldinic acid.** By WILHELM KOENIGS and GEORG JAEGLÉ (*Ber.*, 1895, 28, 1046—1050).—3-Methoxy-4'-phenylquinaldine is formed when the condensation product of acetophenone and paraldehyde is heated with paranisidine, nitrobenzene, and hydrochloric acid. The free base crystallises from benzene in thick tablets melting at 76°. The *hydrochloride* melts at 205·5°, the *sulphate* at 201°, the *picrate* indefinitely at 185—190°, and the nitrate at 169—170° with decomposition. The *platinochloride* melts and decomposes at 232—234°. 3-Hydroxy-4'-phenylquinaldine is formed when the base is boiled with hydrobromic acid. It melts at 248°, and is soluble in both acids and alkalis.

$\gamma$ -Phenylquinaldinic acid can be obtained directly by heating benzoylacrylic acid with aniline, nitrobenzene, and hydrochloric acid; a yield of about 15—20 per cent. of the acid used being obtained.

A. H.

**Constitution of Pyrazolones.** By SIEGFRIED RUHEMANN and ROBERT S. MORELL (*Ber.*, 1895, **28**, 987—989).—In the light of Claisen and Haase's recent research (this vol., i, 193), the authors assign the formulæ  $\begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{NPh}\cdot\text{CO} \end{array} > \text{CMe}\cdot\text{COOEt}$ ,  $\begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{CH}\cdot\text{COOEt}$ , and  $\begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{CH}$ , or  $\begin{array}{c} \text{NH}\cdot\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{CH}$  to the ethylic methylphenylpyrazolonecarboxylate (*Trans.*, 1892, 798), ethylic isopyrazolonecarboxylate, and isopyrazolone (*Abstr.*, 1894, i, 476; this vol., i, 20) prepared by them. The first of these, when treated with hydrochloric acid, yields the corresponding *acid*; this is comparatively stable, and melts and decomposes at 189°. C. F. B.

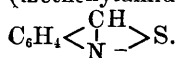
**Antipyrine Patents.** By R. v. ROTHENBURG (*Ber.*, 1895, **28**, 1124).—A reply to Knorr (this vol., i, 396). C. F. B.

**Derivatives of Orthonitrobenzylic Thiocyanate.** By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1025—1029).—Orthonitrobenzylic thiocyanate is converted by ammonium sulphide into orthonitrobenzylic bisulphide, which yields *orthamidobenzylic hydrosulphide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SH}$ , on reduction with tin and hydrochloric acid; its *hydrochloride* melts at 170—172°. This substance is converted by the action of iodine into *orthamidobenzylic bisulphide*, which forms granular crystals, and melts at 90—91°. The *acetyl*-compound crystallises in needles, and melts at 202—205°.

Orthonitrobenzylic thiocyanate is converted by sulphuric acid in the cold into *orthonitrobenzylic carbaminthiolate*,

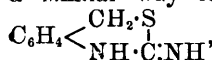


which crystallises in colourless needles, and melts at 115—117°. This substance is converted by reduction into a base, which is an oily liquid, boils at 242—242.5°, and has a characteristic odour, somewhat resembling that of quinoline. The *platinochloride* forms brownish needles. This compound is isomeric with benzothiazole (methenylamidophenyl mercaptan), and is probably *benzisothiazole*,



A. H.

**Halogenised Amines.** By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1029—1038; compare *Abstr.*, this vol., i, 190).—Thiocarbamide reacts with orthamidobenzylic chloride in a similar way to the thiamides, orthobenzylene- $\psi$ -thiocarbamide,



being produced. This substance crystallises from chloroform in lustrous, white, rhombic plates, and melts at 136—137°. It is readily soluble in acids; the *platinochloride* melts at 221—223° with sudden decomposition, and the *picrate* forms yellow needles and melts at 236°. This compound, which has previously been prepared by Cassirer, who gave to it the name thiocyanorthotoluidine, is formed by the reduction of orthonitrobenzylic thiocyanate (*Abstr.*, 1893, i, 16).

When heated with aniline, it yields a product which is identical with the benzophenyldihydrothiometadiazine prepared by Söderbaum and Widman (Abstr., 1890, 178), the constitution of which was proved by Paal and Vanvolxem (Abstr., 1894, i, 621) to be represented by the formula  $C_6H_4 < \begin{smallmatrix} CH_2 \cdot S \\ NH \cdot C : NPh \end{smallmatrix}$ . The same substance is formed by the action of orthamidobenzyl chloride on phenylthiocarbamide.

This view of the constitution of orthobenzylene- $\psi$ -thiocarbamide is borne out by the behaviour of the substance towards oxidising agents. Barium permanganate converts it into the barium salt of an acid substance, the *silver* salt of which has the formula  $C_6H_5N_2O_3SAg$ , and is a colourless microcrystalline powder. This silver salt is decomposed by hydrochloric acid with evolution of sulphurous anhydride, and formation of a base, the *hydrochloride* of which crystallises in lemon-yellow, vitreous prisms. The free *base*,  $C_6H_4 < \begin{smallmatrix} CH \cdot N \\ NH \cdot CO \end{smallmatrix}$ , is an almost white, amorphous mass, and is identical with the quinazolone produced by the condensation of orthamidobenzaldehyde with carbamide.

When the silver salt of the oxidation product of orthobenzylene- $\psi$ -thiocarbamide is treated with silver iodide, methylation, accompanied by elimination of sulphurous anhydride, takes place. The compound produced crystallises in well-developed prisms, melts at  $180^\circ$ , and forms crystalline salts with acids. It is probably a *benzaldehydomethylcarbamide*, but the position of the methyl group has not yet been determined with certainty.

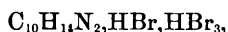
A. H.

**Existence of Coniine in "Sambucus Nigra."** By G. DE SANCTIS (*Gazzetta*, 1895, 25, i, 49—53).—The dilute sulphuric acid extract of the stems and leaves of the common elder (*Sambucus nigra*) contains coniine. The alkaloid was identified by analyses of its salts, and to its presence in the elder is doubtless to be traced the effect which a decoction of the leaves and stems of this tree has on the nervous system.

W. J. P.

**Constitution of Nicotine.** By VINCENZO OLIVERI (*Gazzetta*, 1895, 25, i, 59—77).—On oxidising nicotine in potassium carbonate solution with potassium permanganate, on the water bath, nicotinic, carbonic, oxalic, and acetic acids are formed, together with free nitrogen, and possibly  $\beta$ -hydroxypropionic acid. With the exception of the acid last mentioned, the same products are obtained on oxidising nicotinedibenzylammonium chloride with alkaline permanganate. By the action of acetic chloride on nicotine, a mixture of the alkaloid and its acetyl derivative seems to be obtained.

With bromine, nicotine hydrobromide forms a *perbromide*,



which crystallises in beautiful red needles; it is converted into nicotine by ammonia, and into monobromonicotine by warm dilute

potash. If the hydrobromide is treated with excess of bromine, a *perbromide* of dibromonicotine hydrobromide,  $C_{10}H_{14}Br_2N_2 \cdot HBr, HBr_3$ , is formed; it is a red, viscous mass, which is converted by alcoholic potash into a resin containing a small proportion of dibromonicotine.

On adding iodine solution to nicotine hydriodide, a reddish precipitate separates, which decomposes at  $200^\circ$  with evolution of iodine and methylic iodide, and on distillation with potash yields methylamine. Methylamine and a small proportion of nicotinic acid are obtained on heating nicotine at  $250$ – $280^\circ$  in a closed tube for 24 hours.

The dipiperidyl,  $C_{10}H_{20}N_2$ , obtained by Leibrecht by reducing nicotine with sodium ethoxide, is readily prepared by reducing the base with sodium amyloxyde; it contains two imido-groups, and yields an oily *dinitroso*-derivative with potassium nitrite; an oily *dibenzoyl* derivative can also be prepared, together with a viscous *dicarbamide*,  $C_{10}H_{20}(N \cdot CO \cdot NH_2)_2$ , the *platinochloride* of which forms an amorphous yellow powder, melting and decomposing at  $171^\circ$ .

The author considers that none of the constitutional formulæ hitherto suggested for nicotine satisfactorily explain the various reactions of the alkaloid, and believes that the constitution



which he now proposes, is the most probable one.

W. J. P.

**Methylxanthine, a Product of the Metabolism of Theobromine and Caffeine.** By STANISLAS BONDZYSKI and RUDOLF GOTTLIEB (*Ber.*, 1895, **28**, 1113–1118).—When rabbits, dogs, or men are dosed with theobromine or with caffeine, *monomethylxanthine*,  $C_8H_8N_4O_2$ , appears in the urine. This substance can be obtained crystalline; it melts and decomposes at about  $310^\circ$ , dissolves in 1592 parts of water at  $18^\circ$  and in 109 parts when boiling; in 7575 of absolute alcohol at  $17^\circ$  and in 2250 at the boiling temperature. It yields *silver*, *barium*, and *sodium derivatives*, the last with  $4H_2O$ , one atom of hydrogen in its molecule having been replaced, apparently, by metal.

C. F. B.

**Quinine Hydrochloro-sulphate.** By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1894, [3], **11**, 1138–1139).—The author confirms Grimaux's results (*Abstr.*, 1893, i, 115). Quinine hydrochloro-sulphate is homogeneous, and forms crystals several cm. long; it is exceedingly soluble, and the solution is stable, with the exception that, like solutions of all quinine salts, it slowly absorbs oxygen from the air. On account of its great solubility, the salt affords an excellent means of hypodermically injecting large doses of quinine.

JN. W.

**Constitution of Cinchonine.** By WILHELM V. MILLER and GEORG RHODE (*Ber.*, 1895, **28**, 1056–1077).—The oily compound previously obtained by the action of dilute acetic acid on cinchonine (*Abstr.*, 1894, i, 432), is termed *cinchotoxine*,  $C_{19}H_{22}N_2O$ ; it crystallises slowly below  $0^\circ$  in absence of moisture, and melts at  $58$ – $59^\circ$ . It is a strong base, and liberates ammonia from its salts. The *oxalate* is identical in appearance with cinchonine oxalate. The *hydrogen*



*tartrate* crystallises in colourless concentric needles. The *picrate* and the salts of mineral acids crystallise with difficulty on account of their solubility; various crystalline double salts with zinc chloride, platinum chloride, and mercuric chloride have also been prepared. The only difference between methylcinchonine and methylcinchotoxine is in crystalline habit; they are believed to have the same constitution, and both yield identical derivatives. In physiological properties cinchotoxine and methylcinchotoxine resemble digitoxine, and have no antipyretic action; this characteristic property of cinchonine appears to be caused by the presence in it of a carbon-nitrogen linking, which is resolved in the preparation of cinchotoxine.

Pasteur's cinchonicine, prepared by fusing cinchonine bisulphate, has been obtained in crystals, and is probably identical with cinchotoxine, the only difference yet observed is in crystalline form. *Cinchotoxine phenylhydrazone*,  $C_{25}H_{18}N_4$ , is crystalline, and melts at  $148^\circ$ .

By the action of nitrous acid on cinchotoxine two compounds are formed, which are separated by treatment with soda; the insoluble substance is the *nitroso-derivative*,  $C_{19}H_{21}N_3O_2$ , which crystallises in clear, colourless prisms melting at  $98^\circ$ . It is feebly basic, dissolves in mineral acids, and evolves nitrous anhydride when heated with hydrogen bromide. With phenylhydrazine, it yields two *phenylhydrazones*, melting at  $149^\circ$  and  $163^\circ$  respectively, and a third compound which has not yet been examined. The lower melting hydrazone,  $C_{25}H_{27}N_5O$ , crystallises in concentric prisms, and forms orange-coloured salts with acids. When heated at  $100^\circ$ , it loses 12.19 per cent. of weight; the product is very sparingly soluble, and forms salts which resemble those of the original hydrazone. The second compound from nitrous acid and cinchotoxine has the formula  $C_{19}H_{20}N_4O_3$ , and crystallises in granular aggregates of colourless prisms, melting and decomposing at  $198-199^\circ$ ; it dissolves in alkalis with a yellow colour, and evolves nitrous anhydride when heated with hydrogen bromide.

Cinchotenine reacts like cinchonine with dilute acetic acid; the product has not been isolated, but with phenylhydrazine it yields two phenylhydrazones, the one,  $C_{24}H_{25}N_4O_2$ , crystallises with 3 or 3.5  $H_2O$  in long, slender needles, melts at about  $286^\circ$ , according to the rapidity of heating, dissolves in acids with a reddish-yellow, in alkalis with a yellow, coloration, and is reprecipitated from the latter by carbonic anhydride. The second phenylhydrazone crystallises in rhombic plates, melts at  $196^\circ$ , and is soluble in dilute, but not in concentrated, soda.

As a further guide to the constitution of the cinchonic compounds, the silver salts of dehydrocinchonine and dehydrocinchine were prepared; they are colourless, amorphous, give varying analytical results, and do not resemble the salts of the higher acetylenes described by Krafft and Reuter.

The molecular refraction of cinchotine dihydrochloride = 105.5, that of cinchonine dihydrochloride = 104.81; this indicates that the latter base contains a vinyl, the former an ethyl, group; the theoretical difference in molecular refraction = 0.4 and 2.1 for a vinyl group and a diagonal linking respectively. The molecular

refraction of cinchine = 89.7, that of dihydrocinchine = 88.1, indicating the presence of an acetylene linking in the latter, and of a vinyl group in the former, the calculated difference in molecular refraction = 1.77.

The constitution of cinchonine is fully discussed, and the bearing of Skraup's and Koenigs' recent investigations considered. The conversion of merochinine into  $\gamma$ -methyl- $\beta$ -ethylpyridine renders the author's previous formula for cinchonine improbable; they propose therefore

to substitute for it the following—
$$\text{CMe} \begin{array}{c} \text{CH}(\text{CH}:\text{CH}_2) \cdot \text{CH}_2 \\ \text{C}(\text{OH})(\text{CH}_2\text{C}_9\text{NH}_5) \\ \text{CH}_2 \text{-----} \text{CH}_2 \end{array} \text{N}.$$

J. B. T.

**Alkaloids of Calabar Beans.** By ALEX. EHRENBURG (*Chem. Centr.*, 1894, ii, 439; from *Verh. Vers. deutsch. Naturf. u. Artze.*, ii, 102).—If a salt of eserine (physostigmine) is distilled with solution of caustic alkali in a current of hydrogen, no red colouring matter is produced, but amongst the products of decomposition are methylamine and carbonic anhydride. The residual liquid contains a new base, *eseroline*, which is colourless when crystallised from absolute alcohol, but turns red by the action of moisture. If eserine is heated in a sealed tube with alcoholic ammonia at 150°, eseroline and methylcarbamide are formed, proving the probable formula of eserine to be  $\text{NHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{13}\text{H}_{16}\text{NO}$ . When heated with aqueous alkalis in presence of air, it first yields rubreserine,  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$ , which crystallises in red needles, but which is gradually converted into *eserine-blue*, which is a true dye, colouring silk and wool without mordants.

*Eseridine*, which accompanies eserine, is distinguished from the latter by not yielding rubreserine under the influence of alkalis and air. A third alkaloid isolated by the author, *eseramine*,  $\text{C}_{16}\text{H}_{25}\text{N}_4\text{O}_3$ , crystallises from alcohol in slender, white needles. It is not identical with Harnack's calabarine, as it does not produce tetanus. The author doubts whether calabarine really exists as such in the beans.

L. DE K.

**Apoquinine Derivatives.** By EDUARD LIPPMANN and FRANZ FLEISSNER (*Monatsh.*, 1895, 16, 34–44).—Apoquinine, obtained by the action of dilute hydrochloric acid on quinine (compare Hesse, *Annalen*, 205), is really a mixture of apoquinine, apoquinine hydrochloride, and isomerides of quinine. Approximately, pure apoquinine may be obtained on recrystallising from ether the product formed by heating quinine with dilute hydriodic acid (sp. gr. 1.25–1.35). The base sinters at 160°, melts and decomposes at 210°, and yields the following salts:—A *platinochloride*,  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{PtCl}_6$ , which is a yellow, crystalline powder; an *oxalate*,  $(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2 \cdot 3\text{C}_2\text{H}_2\text{O}_4$ , which crystallises in needles; and an *hydriodide*,  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 \cdot 2\text{HI}$ , which crystallises in yellow prisms. *Ethylapoquinine* is obtained on heating a mixture of apoquinine, sodium ethoxide, and alcoholic ethylic chloride in sealed tubes at 100°. It crystallises in grains and melts sharply at 182°, whereas the isomeric ethylcupreine, or “quinethylin” of Grimaux (*Compt. rend.*, 112, 114), softens at 160°. *Ethylapoquinine platinochloride*,  $\text{C}_{19}\text{H}_{21}\text{EtN}_2\text{O}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , crystallises in pale yellow, flocculent masses.

G. T. M.

## Organic Chemistry.

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### Amalgamated Aluminium as a Neutral Reducing Agent.

By HANS WISLICENUS and LUDWIG KAUFMANN (*Ber.*, 1895, **28**, 1323—1327).—Amalgamated aluminium is prepared by boiling aluminium turnings, freed from oil, with aqueous soda until a copious evolution of hydrogen has set in, rinsing once with water, and acting on the metal for 1—2 minutes with a  $\frac{1}{2}$  per cent. solution of mercuric chloride; the process is then repeated, and the metal finally well washed with water, alcohol, and ether, and kept under light petroleum ready for use. The last traces of water may, after a little while, cause a reaction vigorous enough to raise the petroleum to boiling. This amalgamated aluminium decomposes water with violent evolution of hydrogen; with alcohol or ether, if these contain but slight traces of water, the same reaction occurs; the amalgam has, however, no action on the anhydrous substances. It can thus be used to reduce substances not only in solution in water or aqueous alcohol, but also when dissolved in ether or nearly absolute alcohol, if water be allowed to drop in as required. By the use of this agent exceedingly good results were obtained in the following reductions: ethylic oxalacetate to malate in ethereal solution; nitrobenzene to aniline in aqueous alcoholic solution; nitrobenzene to phenylhydroxylamine in ordinary alcoholic or ethereal solution; 1:2-nitrophenol to 1:2-amidophenol in ordinary alcoholic solution (compare, however, Cohen and Ormandy, *Brit. Ass. Rep.*, 1889, 550).

C. F. B.

### New Class of Compounds of the Inactive Hydrocarbons.

By J. ALFRED WANKLYN and W. J. COOPER (*Chem. News*, 1895, **71**, 250—251).—The authors find that butyric and valeric acids form compounds, similar to the acetic acid compounds, with the hydrocarbons from Russian kerosene (this vol., i, 77) but formic acid does not.

D. A. L.

### Compounds of the Sugars with Alcohols and Ketones.

By EMIL FISCHER (*Ber.*, 1895, **28**, 1145—1167).—The method of preparing glucosides of the alcohols (*Abstr.*, 1894, i, 3 and 565) does not yield satisfactory results with easily decomposable sugars, especially ketoses, besides which the removal of the large quantity of acid employed is, in all cases, troublesome. These difficulties may be surmounted by employing a very dilute solution of hydrogen chloride, and heating for a protracted period, under which circumstances the reaction is just as complete as when the process previously described is made use of.

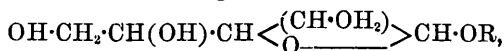
When glucose is dissolved in methylic alcohol containing only 0.25 per cent. of hydrogen chloride, and the solution is heated at 100°,  $\alpha$ - and  $\beta$ -methylglucoside are formed together with a third substance. The latter is most conveniently prepared by shaking anhydrous glucose with 20 parts of methylic alcohol containing 1 per cent. of hydrogen chloride for 10—12 hours, removing the hydrogen

chloride with silver carbonate, evaporating in a vacuum, and extracting with ethylic acetate. It has as yet been obtained only in the form of a colourless, sweet syrup which is very soluble in water and alcohol, but sparingly so in acetone and ethylic acetate; it remains unaltered when heated with Fehling's solution, phenylhydrazine, emulsin, yeast extract, and diastase, but is very easily reconverted into glucose by warm aqueous acids. The author regards the compound as *glucose dimethylacetal*,  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CH}(\text{OMe})_2$ , the analogue of the glucosemeraptals (Abstr., 1894, i, 269). If heated with alcoholic acids, it yields a mixture of  $\alpha$ - and  $\beta$ -methylglucosides.

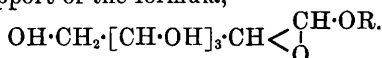
The combination of the sugars with ketones may be brought about by the new method, but attempts failed to effect the combination of the sugars with simple aldehydes on account of the tendency of the latter to polymerisation and condensation.

H. Schiff (Abstr., 1888, 572) obtained certain amorphous compounds of the sugars with aldehydes and ketones, but his views regarding their composition, structure, and properties appear doubtful to the author.

The author's formula for the glucosides,



which is based on the view that these sugar derivatives behave as acetals and not as aldehydes is in best accord with the new observations. Marchlewski, however (Abstr., 1894, i, 104), brings forward arguments in support of the formula,



The author maintains that Marchlewski has overlooked the fact that the conversion of glucosephenylhydrazone into the osazone is accompanied by oxidation, and that the carbinol group is only readily oxidised when it is combined with the hydrazone or aldehyde group. The formation of glucosemeraptals is an argument in favour of the aldehydic constitution of glucose, and there is no reason for assigning any other constitutional formula to this sugar now that it has been shown by Villiers and Fayolle (Abstr., 1894, ii, 489) that, when certain conditions are fulfilled, glucose colours magenta sulphurous acid. Sodium glucosate may well be an hydroxymethylene derivative, and hence its indifference towards phenylhydrazine (Marchlewski, *loc. cit.*). The author finds that, although the neutral aldehydes, as also levulinic acid and salicylaldehyde are readily converted into hydrazones in alkaline solutions, the presence of alkali prevents the formation of benzoylacetone hydrazone. The latter is obtained by treating an ethereal solution of the ketone with phenylhydrazine; it melts and decomposes at 105–110°, reduces Fehling's solution if warmed with it, and when warmed with alcoholic acids is converted into methyldiphenylpyrazole.

*Methyl-d-glucosides* (*loc. cit.*).—When finely pulverised anhydrous glucose (1 part) is dissolved by boiling in 4 parts of anhydrous methylic alcohol, free from acetone, and containing 0.25 per cent. of hydrogen chloride, and the solution is heated in an autoclave at 100°

for 50 hours, and subsequently evaporated to one-third of its volume, the  $\alpha$ -methylglucoside crystallises out after some hours; a further yield of the  $\alpha$ -derivative may be obtained by adding more methyl alcoholic hydrogen chloride to the mother liquor and heating for an additional 40 hours. If, however, it is desired to obtain  $\beta$ -methylglucoside, the first mother liquor is evaporated to a syrup, and placed aside for several weeks to crystallise. When starch is boiled for 15 hours with 10 parts of methylic alcohol containing 1 per cent. of hydrogen chloride, almost complete dissolution takes place, and the liquid, if treated as above described, yields a considerable quantity of  $\alpha$ -methylglucoside. When  $\alpha$ -ethylglucoside is heated at  $100^\circ$  with 10 parts of methylic alcohol containing 0.5 per cent. of hydrogen chloride, it yields a mixture of  $\alpha$ - and  $\beta$ -methylglucoside, conversely  $\alpha$ -methylglucoside may be converted into the ethyl compounds. In the preparation of the compounds which follow, the conditions have to be varied somewhat according to circumstances; in some cases it is necessary to remove the hydrogen chloride by means of silver carbonate.

*Methyl-l-glucosides.*— $\alpha$ -Methyl-l-glucoside prepared by the new method has the same melting point, solubility, and crystalline form as the corresponding derivative of *d*-glucose. The specific rotatory power observed was  $[\alpha]_D = -156.9$ . Equal amounts of the  $\alpha$ -methylglucosides derived from *d*- and *l*-glucose form an optically inactive solution from which crystals having approximately the same melting point,  $163$ — $166^\circ$ , as the optically active glucosides separate. As these crystals could not be measured, it is impossible to decide whether a true racemic compound is formed.  $\beta$ -Methyl-l-glucoside was not obtained quite pure, but the author's preparation had approximately the same melting point as the corresponding derivative of *d*-glucose.

$\alpha$ -Ethyl-d-glucoside crystallises in transparent prisms, melts at  $113$ — $114^\circ$ , and has a specific rotatory power  $[\alpha]_D = +150.5$  at  $20^\circ$ ; it has a sweet taste, and is hydrolysed by yeast extract.

*Methylgalactosides.*—The  $\alpha$ -derivative has the melting point already recorded (*loc. cit.*), but its specific rotatory power is  $[\alpha]_D = +179$  at  $20^\circ$ . Alberda van Ekenstein has privately informed the author that he has obtained  $\beta$ -methylgalactoside. The author finds that the latter compound melts at  $178$ — $180^\circ$  (corr.); it exhibits no distinct optical rotation in 10 per cent. aqueous solution. When dissolved in a cold saturated solution of borax, however, so that a concentration of 8.5 per cent. was obtained, the specific rotatory power was found to be  $[\alpha]_D = +2.6$  at  $20^\circ$ . Unlike the  $\alpha$ -isomeride, it is hydrolysed by emulsin. Besides  $\alpha$ - and  $\beta$ -methylgalactoside, a third compound may be isolated from the mother liquor; it reduces Fehling's solution. It is under investigation.

*Methylglucoheptoside*,  $C_7H_{13}O_7Me$ , crystallises in bunches of small prisms, melts at  $168$ — $170^\circ$ , has a sweet taste, and is almost insoluble in ether; its specific rotatory power is  $[\alpha]_D = -74.7$  at  $20^\circ$ . It is not hydrolysed by yeast extract or emulsin. The isomeric compound was not isolated.

*Methylxylosides*,  $C_5H_9O_5Me$ .—The syrupy reaction product is dissolved in ethylic acetate, when the  $\beta$ -compound crystallises, after a

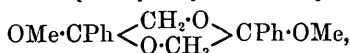
while, from the solution; it melts at 156—157°, tastes sweet, and its specific rotatory power is  $[\alpha]_D = -65.9$  at 20°. *α-Methylxyloside* is obtained from the ethylic acetate mother liquor; it melts at 90—92°, tastes sweet, and its specific rotatory power is  $[\alpha]_D = +152.3$  at 20°. Neither isomeride is hydrolysed by yeast extract or emulsin.

*Methylrhamnoside*,  $C_6H_{11}O_5Me$ , melts at 108—109° tastes bitter, and when heated in small amount distils unchanged. Its specific rotatory power is  $[\alpha]_D = -62.4$  at 20°.

*Methylsorboseide*,  $C_6H_{11}O_5Me$ , crystallises from alcohol or acetone in transparent four-sided plates, melts at 120—122°, and its specific rotatory power is  $[\alpha]_D = -88.7$  at 20°. It is hydrolysed neither by yeast extract nor by emulsin.

*Methylfructoside* was obtained as an amorphous hygroscopic mass; it is reconverted into fructose (levulose) by dilute acids, and also partially hydrolysed in the same manner by yeast extract.

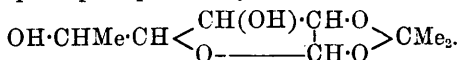
*Methylation of Benzoylcarbinol*.—When to a solution of benzoylcarbinol in methylic alcohol an amount of concentrated hydrochloric acid is added corresponding with 1 per cent. of hydrogen chloride, colourless crystals of a compound which melts at 201° (corr.) separate out. Its constitution is perhaps represented by the formula,



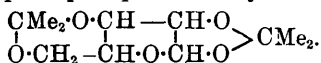
with which analyses and cryoscopic determinations are in accord.

Anhydrous rhamnose has hitherto been obtained only in an amorphous condition; it may, however, be crystallised from dry acetone, from which it separates in the form of needles, and then melts at 122—126°.

*Acetonerhamnoside*,  $C_9H_{16}O_6$ , crystallises in transparent prisms, melts at 90—91°, tastes bitter, and its specific rotatory power is  $[\alpha]_D = +17.5$  at 20°. It does not reduce Fehling's solution and is readily reconverted into rhamnose and acetone by dilute acids. Its constitution is perhaps expressed by the formula,



*Arabinosediactone*,  $C_{11}H_{18}O_5$ , is prepared by dissolving arabinose in dry acetone containing 0.5 per cent. of hydrogen chloride, and shaking the solution for 20 hours. It crystallises in colourless needles, melts at 41.5—43°, is less soluble in warm than in cold water, is volatile with steam, and its specific rotatory power is  $[\alpha]_D = +5.4$  at 20°. Its constitution is perhaps represented by the formula,



*Fructosediactone*,  $C_{12}H_{20}O_6$ , crystallises in long, delicate, glistening needles, melts at 119—120°, tastes bitter, and its specific rotatory power is  $[\alpha]_D = -161.4$  at 20°. An isomeric compound was obtained on one occasion only, and this the author designates *β-fructosediactone*; it melts at 97°, and its specific rotatory power is  $[\alpha]_D = -33.7$  at 20°.

*Glucosediacetone*,  $C_{12}H_{20}O_6$ , is prepared by shaking glucose for 6—8 hours with methylic alcohol containing 1 per cent. of hydrogen chloride, removing the hydrogen chloride, and evaporating in a vacuum, adding acetone and again evaporating to remove the methylic alcohol. The resulting syrup contains a mixture of glucoseacetal and unaltered glucose; it is then shaken with more acetone containing 0.5 per cent. of hydrogen chloride for 10 hours. It crystallises in long, colourless needles, melts at  $107-108^\circ$ , tastes bitter, and is readily hydrolysed by warm dilute aqueous acids. Its specific rotatory power is  $[\alpha]_D = -18.5$  at  $20^\circ$ .

Neither of the acetone derivatives described above is hydrolysed by yeast extract or emulsin.

A. R. L.

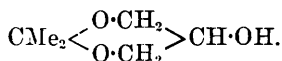
**Combination of Polyhydric Alcohols with Ketones.** By EMIL FISCHER (*Ber.*, 1895, **28**, 1167—1170; compare Abstr., 1894, i, 395 and 438).—The methods adopted in condensing aldehydes with polyhydric alcohols (*loc. cit.*) are no longer applicable when ketones are employed; in such cases, combination is effected by means of very dilute hydrochloric acid.

*Triacetone mannitol*,  $C_{15}H_{26}O_8$ , is obtained by agitating finely powdered mannitol with dry acetone (10 parts), containing 1 per cent. of hydrogen chloride; the operation is carried out at the ordinary temperature, and is continued during 12 hours. The substance crystallises in colourless, slender prisms, and melts at  $68-70^\circ$ ; it has a very bitter taste, and dissolves sparingly in hot water, being very readily soluble in organic solvents. When dissolved in absolute alcohol triacetone mannitol has  $[\alpha]_D = +12.5$  at  $20^\circ$ . Warm dilute hydrochloric acid (0.5 per cent.) quickly resolves it into its components.

*Acetoneglycerol*,  $C_6H_{12}O_5$ , is an odourless liquid, which boils at  $82-83^\circ$  under a pressure of 10—11 mm.; it is miscible in all proportions with water, alcohol, ether, chloroform, and benzene, but is less readily soluble in light petroleum, and is precipitated from aqueous solution by strong alkalis. The sp. gr. = 1.064 at  $20^\circ$ . Warm dilute mineral acids resolve acetoneglycerol into its components, and this result is also produced by benzoic chloride in presence of alkalis.

The resemblance between these compounds and those obtained from aldehydes is so close as to suggest similarity of structure; the constitution of acetoneglycerol, therefore, is probably expressed by

one of the formulæ  $CMe_2 < \begin{matrix} O \cdot CH_2 \\ | \\ O \cdot CH \cdot CH_2 \cdot OH \end{matrix}$  and



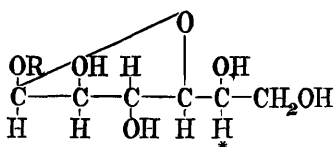
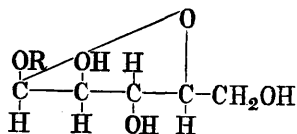
M. O. F.

**Influence of Configuration on the Action of Enzymes.** By EMIL FISCHER (*Ber.*, 1895, **28**, 1429—1438).—It has been rendered evident from the author's previous work that the hydrolysis of glucosides by the enzymes of yeast and by emulsin is dependent on molecular configuration (this vol., i, 6, 161).

When a solution of  $\beta$ -methylgalactoside in water (10 parts) is heated with emulsin (0.2 part) at  $33^\circ$  for three days, about 35 per

cent. is converted into sugar; the behaviour of emulsin towards milk-sugar is similar, and, by analogy, the author considers the latter to be a galactoside of the  $\beta$ -series. Bourquelot (*Bull. Soc. Mycolog.*, 1893, 9, 230) discovered an enzyme in *Aspergillus niger* which hydrolyses maltose, and to which he gave the name maltase. The author proposes for the future to employ the latter term in the place of the word glucase, to denote an enzyme which hydrolyses maltose.

The methyl derivatives of glucoheptose, rhamnose, arabinose, and xylose are quite indifferent towards emulsin and yeast extract. This seems at first surprising in the case of the xylosides, when the similarity of their configuration with that of the *d*-glucosides is borne in mind, thus:—

*d*-Glucoside.

Xyloside.

It therefore appears that the entire configuration of the *d*-glucosides is influenced by the asymmetric carbon atom marked \*. The action of enzymes is limited by structure, for although glucose-ethylmercaptal and the substance which the author regards as glucosemethylacetal (this vol., i, 438) are hydrolysed by acids, they resist the action of emulsin and yeast extract. The question of structure and configuration is much more complicated in the case of the polysaccharides than in that of the glucosides: but the action of enzymes promises to be an important aid to the solution of the problem. The three enzymes—invertase, maltase, and lactase or emulsin bring about the hydrolysis of saccharose, maltose, and milk sugar respectively.

According to Bourquelot (*Abstr.*, 1893, i, 451) invertase is without action on trehalose; the author finds, however, that when trehalose is dissolved in water (10 parts) containing thymol (0.2 part), and treated at 33° for 40 hours with dried Froberg yeast (0.5 part), 20 per cent. of reducing sugar is formed. The diastase prepared from green malt also hydrolyses trehalose, a fact which throws some doubt on the existence of Bourquelot's trehalase from *Aspergillus niger*, since it has long been known that this mould fungus contains a diastatic enzyme, although it should be mentioned that Bourquelot states that his trehalase is rendered inactive at 64°. It seems probable that emulsin and similar substances are mixtures of different enzymes, and this has for some time been considered to be true of diastase. It is also conceivable that the same chemical molecule may be capable of various enzymic functions.

It has lately come to the author's knowledge that Bourquelot (*J. de l'Anat.*, 1886, 180 and 200) showed that maltose is hydrolysed if an aqueous solution be treated with yeast in presence of chloroform for 3–8 days, and he concluded from this that maltose is hydrolysed prior to fermentation. Lintner (*Zeit. ges. Brauw.*, 1895, 106) also



stated that maltose is hydrolysed by yeast. Morris (Proc., 1895, 46) has confirmed the author's observation as regards the action of dried or ruptured yeast cells on maltose, but finds that fresh Froberg yeast has no action on a solution of maltose in presence of chloroform. The author now shows that the absence of action is not due to the degree of moisture, but is conditioned, to a great extent, by the chloroform; thus, little or no change is found to occur when maltose or  $\alpha$ -methylglucoside is treated with Froberg or Saaz yeast in presence of chloroform; considerable hydrolytic action is observed, however, in the case of both compounds when they are treated with the yeasts in presence of 0.2 per cent. of thymol or 0.3 per cent. of toluene, as also when the aqueous solutions are saturated with ether, and the vessel (test tube) in which the experiment is performed is left open so that the ether can evaporate. In the case of  $\alpha$ -methylglucoside, the glucose produced was estimated by titration with Fehling's solution, whilst in that of maltose it was estimated as glucosazone as follows:—The liquid filtered from the yeast is heated on a water bath to precipitate the proteids, and 10 per cent. of crystallised sodium acetate added. To the filtrate (5 c.c. of a 10 per cent. solution) pure phenylhydrazine (1 gram) and 50 per cent. acetic acid (1 gram), together with a volume of water equal to that of the total liquid are added. The mixture is now heated in a water bath for  $1\frac{1}{4}$  hours. The osazone, after remaining for an hour at the temperature of the room, is collected on a filter, washed with cold water, and well boiled with 50 c.c. of water; it is then filtered while hot, washed with hot water, dried at  $100^{\circ}$ , and weighed. The phenylhydrazine employed ought to dissolve to a clear solution in 2 per cent. acetic acid; it should be kept in hermetically sealed vessels. The amount of glucosazone produced being dependent on the concentration of the solution, the quantity of phenylhydrazine, and the presence of other sugars, is only an approximate method for the estimation of glucose, but qualitatively the osazone test is to be preferred to all other methods.

From these experiments, it is clear that the enzyme which hydrolyses maltose and  $\alpha$ -methylglucoside is not formed by drying the yeast, and inasmuch as its production by the action of thymol, toluene, or ether is inconceivable, it must be concluded that it is present in normal yeast. The drying of the yeast simply permits the extraction of the enzyme by water. So long as the yeast is quite fresh and moist, hydrolysis occurs only within the cells, as the maltase, even in presence of the above-named anæsthetic agents, does not pass into solution.

A. R. L.

**Action of Potassium Permanganate on various Carbon Compounds.** By EDMÉ J. MAUMENÉ (*Compt. rend.*, 1895, 120, 783—785).—Manganic oxide, prepared by the action of sugar on potassium permanganate in aqueous solution, is soluble in concentrated aqueous solutions of sugar, the solubility increasing rapidly with the proportion of sugar. The manganic oxide is gradually reduced to manganous oxide, and the sugar is oxidised to an acid. When equal weights of manganic oxide and sugar are dissolved in eight or ten times their

weight of water, and boiled for some time, the product is the acid  $C_6H_{12}O_7$ .

The two acids,  $C_6H_{12}O_8$  and  $C_3H_6O_5$ , obtained by the action of permanganate on sugar, when dissolved in water in the form of potassium salts, are gradually oxidised by manganic oxide, and yield lactic and formic acids. This fact probably explains the divergence between the author's results (this Journal, 1872, 812) and those of subsequent observers.

C. H. B.

**Carbohydrates prepared from Formaldehyde.** By TRASABURO ARAKI (*Pflüger's Archiv*, 1895, 60, 261—262).—An answer to Loew (this vol., i, 164). Polemical.

W. D. H.

**Chitosan.** By TRASABURO ARAKI (*Zeit. Physiol. Chem.*, 1895, 20, 498—510; compare Hoppe-Seyler, this vol., i, 166, 167).—Chitosan has the composition  $C_{14}H_{26}N_2O_{10}$ , and its formation from chitin is represented by the equation  $C_{18}H_{30}N_2O_{12} + 2H_2O = C_{14}H_{26}N_2O_{10} + 2C_2H_4O_2$ , as was shown by a quantitative study of the reaction, in which the chitosan was weighed as such, the acetic acid as the barium salt. When heated at  $110^\circ$ , chitosan decomposes, mainly according to the equation  $C_{14}H_{26}N_2O_{10} + 2H_2O = 2C_6H_{13}NO_5 + C_2H_4O_2$ ; but secondary reactions also occur, for glucosamine and acetic acid are not the only products; some formic acid is also formed. When it is heated with acetic anhydride at  $135^\circ$ , it yields a derivative which resembles chitin in its properties, but contains at least three acetyl-groups—one more than that substance. It is noteworthy that the texture of the original chitin, from the carapace of the lobster, is retained in all these compounds; chitin can be converted into chitosan, this into its acetyl derivative, and this back again into chitosan, without the form of the substance, or even its microscopic structure, being altered. Chitosan is coloured violet by dilute iodine solution; its acetyl derivative and chitin are not. The author agrees with Winterstein (this vol., i, 199), that the tissues of fungi contain a substance very closely allied to chitin.

C. F. B.

**Hexamethylenetetramine Compounds.** By MARCEL DELÉPINE (*Compt. rend.*, 1895, 120, 743—745).—The compound,  $C_6H_{12}N_4 \cdot 2HgCl_2 + H_2O$ , is obtained in silky needles by mixing cold aqueous solutions of its proximate constituents; whilst in hydrochloric acid solutions,  $C_6H_{12}N_4 \cdot HCl \cdot 2HgCl_2 + H_2O$  is also obtained in silky needles. The former melts at about  $208^\circ$ , and the latter at  $165^\circ$ , and both combine with two atomic proportions of bromine.

The compound,  $C_6H_{12}N_4 \cdot 2HgCl_2 + NH_4Cl \cdot 2HgCl_2 + 3H_2O$ , is found in concentrated solutions in presence of ammonium chloride, and forms hard, transparent, prismatic crystals which combine with two atoms of bromine for each molecule of the amine.

All these compounds, when boiled with water, yield yellow mercuric oxide, ammonium chloride, and formaldehyde.

With phenylhydrazine hydrochloride, hexamethylenetetramine yields the crystalline compound,  $C_{15}H_{16}N_4$ , obtained by Wellington and Tollens from phenylhydrazine and formaldehyde (Abstr., 1886,

330); and since ammonia is present in the mother liquor, it seems probable that the hexamethylenetetramine first splits up into ammonia and formaldehyde. The formation of the compound is, however, much less rapid than with formaldehyde alone. C. H. B.

**Methylnitramine.** By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1894, **13**, 308—330).—Methylnitramine is reduced by zinc dust to methylic alcohol and nitrogen. As no methylhydrazine is formed, and as the amount of zinc used is much less than that required to form the latter, it is probable that methylamine and nitrous acid are the first products, and that the alcohol and nitrogen are due to their mutual action; small quantities of these intermediate products can, in fact, be detected. With sodium amalgam in alkaline solution, the main action is the same, but some hydroxylamine is probably also formed.

The acid properties of methylnitramine are rather stronger than those of carbonic acid, as it displaces the latter from its salts. The *ammonium*, *silver*, *zinc*, *cadmium*, *mercury*, and *copper* salts are crystalline; the *barium* salt crystallises with 1 mol.  $\text{H}_2\text{O}$ ; the *lithium*, *calcium*, and *magnesium* salts could not be crystallised. The copper and zinc salts are decomposed by water into *basic* salts and the free nitramine, in this resembling the carbonates; but the silver and mercuric salts are quite stable.

The alkylic salts are prepared by acting on an alcoholic potash solution of the potassium salt with the alkylic bromide in closed vessels at  $100^\circ$ . *Methylethynitramine*,  $\text{NMeEt}\cdot\text{NO}_2$ , the molecular weight of which was determined by the vapour-density method, melts at  $-30^\circ$  and boils at  $195.7^\circ$ ; sp. gr. = 1.100 at  $15^\circ$ ; it is insoluble in water, and, in accordance with van Erp's rule, is hydrolysed by caustic alkalis into ethylamine and formic and nitrous acids. *Methylpropylnitramine* boils at  $115$ — $116^\circ$  (40 mm.), or at  $208$ — $210^\circ$  (atmos.), in the latter case decomposing partially; sp. gr. = 1.063 at  $15^\circ$ . *Methylisopropylnitramine* boils at  $60$ — $61^\circ$  (40 mm.). J. N. W.

**Action of Nitric Peroxide on Ketoximes.** By ROLAND SCHOLL and GEORG BORN (*Ber.*, 1895, **28**, 1361—1368; compare Abstr., 1888, 443).—When pinacoloxime,  $\text{CMe}_3\cdot\text{CMe}\cdot\text{NOH}$ , is treated in ethereal solution with nitric peroxide, *pinacolininitrimine*,  $\text{CMe}_3\cdot\text{CMe}\cdot\text{N}\cdot\text{NO}_2$ , is formed as a colourless oil which boils at  $81$ — $83^\circ$  (at 10 mm. pressure). This substance has not the characteristic properties of a nitroso-compound, and is not altered by boiling with sodium ethoxide in alcoholic solution, so that the formula given is most probably correct. When it is treated with hydroxylamine hydrochloride, it is reconverted into pinacolinoxime. Oxidation with chromic acid and acetic acid converts the nitrimine into a white, crystalline substance of the formula  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2$ , which has only been obtained in exceedingly small quantity. It melts at  $172^\circ$ , and is very volatile, subliming at the ordinary temperature. Its formula shows that it cannot be a dinitromethane derivative such as  $\text{CMe}(\text{NO}_2)_2\cdot\text{CMe}_3$ , and this is a further proof that the constitution of the nitrimine is not represented by the formula  $\text{CMe}_3\cdot\text{CMe}(\text{NO})_2$ .

Acetoxime is converted by nitrogen peroxide in ethereal solution into propylpseudonitrole and a substance which is probably *tetra-methyldinitroazoxymethane*,  $O < \begin{smallmatrix} \text{NCMe}_2\text{NO}_2 \\ | \\ \text{NCMe}_2\text{NO}_2 \end{smallmatrix}$ . The latter, which is only formed in small quantity, separates from ether in colourless, rhombohedral crystals, which are odourless and melt at  $97^\circ$ . A. H.

**Aldehydes of the Acetic Series.** By LOUIS HENRY (*Compt. rend.*, 1895, **120**, 837—840).—In the aldehydes of the acetic series the group CHO is a smaller fraction of the molecule the higher the molecular weight, and it would seem to follow that the energy of the aldehydic function should diminish as the molecular weight increases. This is well seen in the tendency to polymerise, which is most marked in the case of formaldehyde, and decreases as the molecular weight increases. A similar change is observed in the energy with which the aldehydes interact with alkylamines, and in the tendency of the products, which will be described subsequently, to polymerise. The reaction between the aldehydes and the amines is also more energetic the lower the molecular weight of the amine, or in other words, the higher the ratio of the  $\text{NH}_2$ -group to the rest of the molecule. The tendency of the products (the aldehydic amines) to polymerise, also diminishes with an increase in the molecular weight of the alkylic radicle of the amine.

The boiling points of these aldehydic amines are, as a rule, almost identical with those of the corresponding dialkylamines. The elimination of a molecule of hydrogen in the system  $\text{HC}\cdot\text{NH}$ , with production of double linking between carbon and nitrogen  $>\text{C}\cdot\text{N}-$ , has very little effect on the volatility. C. H. B.

**Preparation of Thioacetic acid.** By ROBERT SCHIFF (*Ber.*, 1895, **28**, 1204—1206).—See this vol., ii, 370.

**Protein-like Substances.** By LEON LILIENFELD (*Chem. Centr.*, 1894, ii, 478; from *Du Bois-Reymond's Archiv.*, 1894, 383—386).—If ethylic amidoacetate is heated with potassium hydrogen sulphate for some time on the water bath, a base, *biuretdimethylene*,



is formed, the *carbonate* of which,  $\text{C}_6\text{H}_3\text{N}_3\text{O}_4$ , was obtained crystallised. When this is heated with water, a substance is formed which has the physical properties and percentage composition of gelatin.

Ethylic amidocaproate is a yellow liquid; ethylic hydroxyphenylamidopropionate a crystalline solid. These, and also ethylic aspartate, condense with the above-mentioned base, yielding products which exhibit the reactions of proteids. C. F. B.

**The Drying of Fats.** By ACH. LIVACHE (*Compt. rend.*, 1895, **120**, 842—845).—Non-drying oils, when treated with manganese or lead oxides or salts and exposed to the air in thin layers, do not dry even after several months' exposure. If, however, non-drying oils or fats, solid or liquid, are heated at  $120$ — $160^\circ$ , either alone or in presence of

lead or manganese compounds, in such a manner as to expose a large surface to the air, drying takes place somewhat rapidly—especially if the metallic compounds are present.

The product obtained is yellow, transparent, very elastic, swells up in ether, benzene, alcohol, &c., without dissolving, and is easily saponified by alkalis. It seems, therefore, to be identical with the linolin obtained from drying oils and fats; but this point is under investigation.

The classification of vegetable oils into drying and non-drying oils is well defined at the ordinary temperature, but at a higher temperature the distinction disappears, and all oils and fats, whether of animal or vegetable origin, yield a solid product if heated for a sufficient length of time at a suitable temperature. C. H. B.

**Undecanonic acid.** By E. WELANDER (*Ber.*, 1895, **28**, 1448—1450).—Undecolic acid,  $C_{11}H_{18}O_2$ , is best prepared by heating the dibromide of undecylenic acid with concentrated aqueous potash at  $180^\circ$ . *Ethyl undecolate*,  $C_{11}H_{17}O_2Et$ , boils at  $197^\circ$  (at 49 mm. pressure). *Undecanonic acid*,  $COMe[CH_2]_8COOH$ , (?) is obtained by treating undecolic acid with sulphuric acid. It crystallises from boiling water in plates which melt at  $49^\circ$ . The *oxime*,  $C_{11}H_{20}O_2NOH$ , is an oil, and the *silver* salt a white precipitate. A. H.

#### **Oxidation of Ethylic Isonitrosoacetoacetate with Nitric acid.**

By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 1213—1217; compare *Abstr.*, 1892, 699).—Cramer has shown (*loc. cit.*) that the compound obtained by Pröpper from ethylic acetoacetate and nitric acid is formed by elimination of  $2H_2O$  from 2 mols. of ethylic oximidoacetate, and has

the constitution  $\begin{array}{c} O:N:C\cdot COOEt \\ | \\ O:N:C\cdot COOEt \end{array}$ . The author has oxidised ethylic isonitrosoacetoacetate with nitric acid, obtaining, together with acetic acid, a compound of the formula  $NO_2\cdot C(NO_2)\cdot COOEt$ , for which the name ethylic oximidonitroacetate or ethylic acetate-nitrolic acid is suggested; this result is analogous to the formation of acetylmethylnitrolic acid on treating isonitrosoacetone with nitric acid.

*Ethylic oximidonitroacetate* is obtained by dissolving ethylic isonitrosoacetate in nitric acid (sp. gr. 1.2); the liquid is cooled during solution, and when the reaction is finished, treated with twice or thrice its volume of water. Ether extracts the substance, which crystallises in large prisms, and melts at  $69^\circ$ , decomposing at a slightly higher temperature. The compound is more stable in the atmosphere than when preserved in the desiccator, the nitrous acid which arises from its decomposition being free to escape without having further action on the substance. It is decomposed by alkalis, developing a reddish-yellow coloration, and water also attacks it; the substance dissolves very readily in ether and alcohol, but is insoluble in light petroleum. It has an irritating effect on the eyes, and attacks the skin vigorously.

The action of nitric acid on ethylic isonitrosoacetoacetate also gives rise to the compound obtained by Pröpper, to which reference has been already made, and this is separated from ethylic oximidonitroacetate

by decomposing the latter with sodium carbonate, which is without effect on the compound in question; it is also formed on heating ethylic oximidonitroacetate at 70—75°, or allowing it to remain in closed vessels for several weeks.

When ethylic oximidonitroacetate remains in contact with concentrated hydrochloric acid for 24 hours, ethylic chloroximidoacetate is formed.

M. O. F.

**Ethylic  $\beta$ -Amidoanticrotonate.** By RENÉ THOMAS-MAMERT (*Bull. Soc. Chim.*, 1895, [3], 13, 68—72).—To decide whether the product of the action of ammonia on ethylic acetoacetate is an amido-crotonate or an imidobutyrate, ethylic  $\beta$ -amidocrotonate was made from the corresponding chloro-compound. Ethylic  $\beta$ -chloranticrotonate is conveniently prepared by the action of phosphorus pentachloride on ethylic acetoacetate in benzene solution; after removal of the reagent and solvent, the product consists of a mixture of the two stereoisomeric salts, but the syn-compound can be converted into its isomeride by boiling with iodine. The amido-compound obtained by heating the chlorocrotonate with alcoholic ammonia at 100° yields the acetyl derivative described by Collie (*Abstr.*, 1887, 501), and is identical in physical and chemical properties with the product of the action of ammonia on ethylic acetoacetate. The latter, therefore, is ethylic  $\beta$ -amidoanticrotonate. The corresponding methylic salt, prepared in a similar manner, is identical with that described by Conrad and Epstein (*Abstr.*, 1888, 253).

Since anticrotonic (isocrotonic) acid is related to acetoacetic acid, it must be a stereoisomeride of crotonic acid, and Fittig's formula (*Annalen*, 226, 309)  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ , must be rejected.

JN. W.

**Rotatory Power of Alkylic  $\beta$ -Methyladipates.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1895, [3], 13, 6—10).—A further instalment of the work on the validity of Guye's formula, and on the influence of solvents on rotatory power (compare this vol., i, 173, 210, 267).

$\beta$ -Methyladipic acid ( $\gamma$ -pimelic acid) is best prepared by oxidising menthone with neutral permanganate, and may be extracted with ether from the clear, acidified product after saturation with ammonium sulphate; the menthone is conveniently prepared from menthol by oxidation with chromic acid. The pure acid crystallises in colourless plates, and melts at 91—92°, not at 89·5°, as stated by Manasse and Rupe (*Abstr.*, 1894, i, 470); it boils undecomposed at 211° under 21 mm. pressure, but under ordinary pressure is partially converted into the anhydride (compare, however, the authors cited); the specific rotatory power in 2 per cent. aqueous solution is  $[\alpha]_D = +8\cdot4^\circ$ .

The alkylic salts are readily prepared by the hydrogen chloride method. The *methylic* salt is a colourless, mobile liquid, having a faint, fruity odour, and boiling at 134—135° (40 mm.); sp. gr. = 1·008 at 18°; the specific rotatory power is  $[\alpha]_D = +0\cdot6$ . The *ethylic* salt (compare Semmler, *Abstr.*, 1893, i, 130) boils at 127° (10 mm.), or at 165—170° (50 mm.); sp. gr. = 0·998 at 18°; the specific rota-

tory power of the liquid is  $[\alpha]_D = -0.9$ , of the 6 per cent. benzene solution  $[\alpha]_D = -1.0^\circ$ .

The change of sign of the rotatory power in passing from the acid through the methylic salt to its higher homologue is not predicted by Guye's formula; it may be, however, that the length of the substituted chains has reached in these compounds the limiting point beyond which the free rotation required by Guye's hypothesis is no longer possible.

As regards the influence of solvents on the physical properties of the dissolved substance, the author's view that polarimetric and cryoscopic anomalies are due to a common cause, namely, a peculiar kind of dissociation (this vol., ii, 194), is completely borne out by the behaviour of ethylic  $\beta$ -methyladipate. The structure of the alkyladipates does not admit of the peculiar dissociation to which the acidyltartrates may be considered liable, and their polarimetric and cryoscopic properties should therefore be independent of the solvent; in the only compound of the series that has been fully examined, namely, this ethylic salt, this is the case. The author is now studying the higher homologues. JN. W.

#### **Ketonic Compound from Tartaric acid: Parapyruvic acid.**

By EDUARD MULDER (*Rec. Trav. Chim.*, 1894, 13, 345—402; compare *Abstr.*, 1893, i, 685).—The products, respectively soluble and insoluble in acetic acid, which result from the action of ethylic chloride on ethylic disodiotartrate, have now been proved to yield acetic and oxalic acids, and a modification of pyruvic acid. The insoluble compound is probably ethylic sodiotartryltartrate, and the soluble compound, ethylic sodioethyltartryltartrate. Tartryltartaric acid can be resolved into acetic and oxalic acids, or into carbonic and glyceric acids. The pyruvic acid might readily arise from the latter by simple dehydration.

The soluble substance mentioned above seems to form a loose, colloidal compound with sodium chloride. In connection with this, it is noteworthy that barium tartrate and oxalate, when precipitated in the presence of pyruvic acid, are amorphous and gelatinous, and readily dissolve, and remain dissolved, in acetic acid, whereas, when precipitated alone, as is well known, they soon become crystalline and insoluble. These facts may prove of importance in vegetable physiology. JN. W.

#### **Resolution of Pyrotartaric acid into its Optical Components.**

By ALBERT LADENBURG (*Ber.*, 1895, 28, 1170—1171).—Pyrotartaric acid, melting at  $117-118^\circ$ , was converted into the strychnine salt, which melts at  $186^\circ$ ; this yields a specimen of the acid which melts at  $115^\circ$ . On repeating this operation, dextro-rotatory pyrotartaric acid is isolated, whilst the lævo-modification may be obtained from the mother liquors of the strychnine salt.

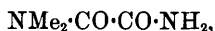
M. O. F.

#### **Amido-derivatives of Oxalic acid.**

By ANTOINE P. N. FRANCHIMONT and H. A. ROUFFAER (*Rec. Trav. Chim.*, 1894, 13,

331—344).—Of the five methyloxamides, only the mono- and symmetrical di-derivatives are accurately known. Tetramethyloxamide is prepared by a method analogous to that used by Hammerich (Abstr., 1892, 1084) in preparing the corresponding tetrabenzyl compound, namely, by acting with sodium on *dimethylcarbamic chloride* in ethereal solution. This chloride is best prepared by the action of carbonic chloride on dimethylamine in benzene solution; it melts at  $-33^{\circ}$ , and boils at  $167-167.5^{\circ}$  ( $754.7$  mm.); sp. gr. =  $1.174$  at  $15^{\circ}$ . *Tetramethyloxamide*,  $\text{NMe}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NMe}_2$ , crystallises in long, white needles, and melts at  $80^{\circ}$ ; it is sparingly soluble in ether, but freely in chloroform and benzene, and is not appreciably attacked by nitric acid; it is hydrolysed by baryta water into *barium dimethyloxamate*, which is very soluble in water; the free acid crystallises from chloroform and benzene in long, flat needles or prisms, and melts at  $130^{\circ}$ , decomposing at a higher temperature into carbonic anhydride and *dimethylformamide*,  $\text{H}\cdot\text{CO}\cdot\text{NMe}_2$ . This is a colourless liquid, which boils at  $153^{\circ}$  (corr.), and remains liquid even at  $-55^{\circ}$ ; sp. gr. =  $0.9525$  at  $15^{\circ}$ .

*Dimethyloxamamide*, (unsymmetrical dimethyloxamide),



prepared from ethylic dimethyloxamate in the usual way by the action of ammonia, crystallises from benzene in small, square plates, and melts at  $104^{\circ}$ ; it can be distilled unchanged under very low pressure, and is converted by nitric acid into nitrous oxide, carbonic oxide and anhydride, and dimethylamine. Ethylic oxalate melts at  $-41^{\circ}$ ; it is converted by aqueous dimethylamine into *dimethylammonium oxalate*, but by the dry amine into ethylic dimethyloxamate; the latter melts at  $-22^{\circ}$ , and boils at  $241-242^{\circ}$ , or at  $129.5^{\circ}$  ( $18$  mm.); sp. gr. =  $1.081$  at  $15^{\circ}$ .

*Trimethyloxamide* is obtained from this by the action of methylamine, and is separated from the solid symmetrical dimethyloxamide, which is formed at the same time (apparently by direct replacement of a dimethylamido- by a methylamido-group), partly mechanically, and partly by fractionation under low pressure; it crystallises in oblique rhombic plates, and is extremely hygroscopic; it melts at about  $32^{\circ}$ , and boils at  $139^{\circ}$  ( $22$  mm.). JN. W.

**Optically Active Halogen Derivatives.** By PAUL WALDEN (*Ber.*, 1895, **28**, 1287—1297; compare Abstr., 1893, i, 250).—*d*-Chlorosuccinic chloride,  $\text{COCl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{COCl}$ , boils at  $91-93^{\circ}$  ( $11$  mm. pressure), and has the specific rotation  $[\alpha]_D = +29.53^{\circ}$ . *d*-Chlorosuccinic anhydride may be prepared by shaking the acid with phosphoric anhydride and distilling in a vacuum. It melts at  $80^{\circ}$ , and has the rotation  $[\alpha]_D = +30.85^{\circ}$  in solution in ethylic acetate. *Dimethylic d-chlorosuccinate* is obtained by the action of phosphorus pentachloride on dimethylic malate in chloroform solution. It boils at  $107^{\circ}$  ( $15$  mm. pressure), and has the rotation  $[\alpha]_D = +41.40^{\circ}$ . *Diethylic d-chlorosuccinate* may be obtained by the etherification of chlorosuccinic acid with alcohol and hydrogen chloride. It boils at  $131^{\circ}$  ( $18$  mm. pressure), and has the rotation  $[\alpha]_D = +27.50^{\circ}$ .



The action of phosphorus pentabromide on free malic acid is very slow and incomplete, whilst it acts very readily on the ethereal salts. *Dimethylic d-bromosuccinate* boils at  $129^{\circ}$  (23 mm. pressure), and has the rotation  $[\alpha]_D = +50.83^{\circ}$ . *Diethylic d-bromosuccinate* boils at  $143^{\circ}$  (28–30 mm. pressure), and has the rotation  $[\alpha]_D = +40.96^{\circ}$ .

*Ethylic l-chloromalate* is obtained by the action of phosphorus pentachloride on ethylic d-tartrate. It boils at  $162\text{--}165^{\circ}$  (15 mm. pressure), has sp. gr. = 1.2543 (at  $20^{\circ}/4^{\circ}$ ), and the rotation  $[\alpha]_D = -8.05^{\circ}$ . The fact that this compound is lævorotatory must be taken to show that it contains two asymmetric carbon atoms, since simple partial reduction of d-tartaric acid yields d-malic acid. *Ethylic l-bromomalate* boils at  $165\text{--}168^{\circ}$  (12–15 mm. pressure), and has sp. gr. = 1.4330, and the rotation  $[\alpha]_D = -2.44^{\circ}$ .

*Methylic d-chloropropionate*,  $\text{CHMeCl}\cdot\text{COOMe}$ , is obtained by pouring the product of the action of phosphorus pentachloride on sarcolactic acid into methylic alcohol. It boils at  $132\text{--}134^{\circ}$ , and has sp. gr. = 1.1520, and the rotation  $[\alpha]_D = +19.01^{\circ}$ . The corresponding inactive compound, prepared from inactive lactic acid, has the same boiling point and a density of 1.1515. *Ethylic d-chloropropionate* boils at  $146\text{--}149^{\circ}$ , has sp. gr. = 1.0888, and the rotation  $[\alpha]_D = +12.86^{\circ}$ . The corresponding inactive compound has the same boiling point, and sp. gr. = 1.0869.

*Ethylic d-bromopropionate* is formed in small amount by the action of phosphorus pentabromide on ethylic d-lactate. It boils at about  $162^{\circ}$ , and has the rotation  $[\alpha]_D = +7.18^{\circ}$ . The corresponding inactive salt has the same boiling point and index of refraction  $n_D = 1.447$ .

*d-Phenylacetic chloride*, prepared from mandelic acid, boils at  $120^{\circ}$  (23 mm. pressure), and has the rotation  $[\alpha]_D = +158^{\circ}$ . The free acid melts at  $56\text{--}58^{\circ}$ , and has the rotation  $[\alpha]_D = +132.13$  in benzene solution. *Ethylic d-phenylchloracetate* boils at  $162^{\circ}$  (45 mm. pressure), has sp. gr. = 1.1594, and the rotation  $[\alpha]_D = +25.19^{\circ}$ . *Propylic d-phenylchloracetate* boils at  $180^{\circ}$  (60 mm. pressure), has sp. gr. = 1.1278, and the rotation  $[\alpha]_D = +23.94^{\circ}$ .

*d-Phenylbromacetic bromide* boils at  $145\text{--}147^{\circ}$ , and has sp. gr. = 1.853, and the rotation  $[\alpha]_D = +44.53^{\circ}$ . The acid melts at  $76\text{--}78^{\circ}$ , whilst the inactive acid melts at  $83\text{--}84^{\circ}$ . *Ethylic d-phenylbromacetate* boils at  $164^{\circ}$  (20 mm. pressure), has a most violent action on the mucous membrane, and has sp. gr. = 1.3893, and rotation  $[\alpha]_D = +16.56^{\circ}$ . *Isobutylic d-phenylbromacetate* boils at  $167\text{--}168^{\circ}$  (19 mm. pressure), has sp. gr. = 1.2892, and the rotation  $[\alpha]_D = +9.77^{\circ}$ .

These results seem to show that the optical activity of a carbon atom depends simply on the existence of a difference between the four groups with which it is combined, whilst the nature of the groups only influences the direction and amount of the rotation produced.

A. H.

**Action of Boron Fluoride on Organic Compounds.** By V. GASSELIN (*Ann. Chim. Phys.*, 1894, [7], 3, 5–83).—In preparing boron fluoride care must be taken that the fluor-spar used does not

contain much silica. The gas is best prepared by dissolving boric anhydride in hot concentrated sulphuric acid, cooling the solution, adding the finely powdered calcium fluoride, and heating at 125—130°. The gas then comes off very regularly and steadily.

No action could be obtained with carbonic oxide or with methane.

Cold methylic alcohol absorbs exactly one molecular proportion of boron fluoride, and forms *boron methoxydifluoride*,  $\text{BF}_2 \cdot \text{OMe}$ . This compound crystallises in prisms, melts at 41.5°, and boils at 87°. It dissolves readily in methylic and ethylic alcohols, but the solutions gradually decompose with formation of the borates. With water or alkalis, it decomposes readily, according to the equation  $2\text{BF}_2 \cdot \text{OMe} + 3\text{H}_2\text{O} = 2\text{MeOH} + \text{B}(\text{OH})_3 + \text{HBF}_4$ . Sodium is without action on this compound even at 100°. Sodium methoxide acts on it readily; if molecular proportions are employed *boron dimethoxyfluoride*,  $\text{BF}(\text{OMe})_2$ , is formed. This is a colourless mobile liquid, fuming in the air, and burning with a green flame. It boils at 53°, and has sp. gr. = 1.053 at 0°. Water and alkalis decompose it in like manner to the difluorine compound. Sodium methoxide yields methylic borate,  $\text{B}(\text{OMe})_3$ . As this compound is not well known, it was carefully purified and examined. It is a colourless liquid, which boils at 55—56°, has sp. gr. = 0.919 at 0°, and burns with a green flame. It decomposes rapidly in moist air or with water.

Dry methylic borate absorbs boron fluoride readily, with development of heat, and the re-formation first of  $\text{BF}(\text{OMe})_2$  and finally of  $\text{BF}_2 \cdot \text{OMe}$ . The yield of these two compounds is much nearer the theoretical in this mode of formation than by the action of boron fluoride on methylic alcohol. In the latter reaction, a large part of the product passed over between 120—130°, and proved to be a *molecular compound* of boron fluoride and methylic oxide,  $\text{BF}_3 \cdot \text{OMe}_2$ . This is a colourless liquid, which fumes in air, and is decomposed by water, with evolution of methylic oxide. It boils at 126—127°, but dissociation takes place at this or a slightly higher temperature, as the vapour density (at the temperature of boiling aniline) gave 2.03 (theory 3.96). This compound is also readily formed, with development of heat, by the direct union of boron fluoride and methylic oxide. Its sp. gr. at 0° is 1.140. The product of still higher boiling point obtained in the action of boron fluoride on methylic alcohol contains an oily acid. Under a pressure of 3 mm. of mercury a fraction boiling at 92°, and of sp. gr. = 1.574 at 12° was obtained, giving figures approximately corresponding with the formula  $\text{BF}_3 \cdot \text{O}_2\text{H}_4$ . With potash, it yielded a salt,  $\text{BF}_2(\text{OH}) \cdot \text{KF}$ . Excess of potash yields a mixture of potassium borofluoride,  $(\text{KBF}_4)$ , potassium fluoride, and potassium borate. It is doubtful whether the compound  $\text{BF}_2(\text{OH}) \cdot \text{HF}$  exists in the free state, or whether that and also the more or less similar compounds said to have been obtained by previous workers are not really only mixtures of boron fluoride, hydrofluoric and boric acids, &c.

With ethylic alcohol, boron fluoride reacts in the same way as with methylic alcohol. *Boron ethoxydifluoride*,  $\text{BF}_2 \cdot \text{OEt}$ , crystallises in prisms, melts at 23° and boils at 82°. *Boron diethoxyfluoride*,  $\text{BF}(\text{OEt})_2$ , boils at 78°, and has sp. gr. = 1.054 at 0°. The *molecular compound*,  $\text{BF}_3 \cdot \text{OEt}_2$ , boils at 123°. Ethylic borate,

$\text{B}(\text{OEt})_3$ , boils at  $118\text{--}119^\circ$ , and has sp. gr. =  $0.887$  at  $0^\circ$ , as found by Schiff and Bechi.

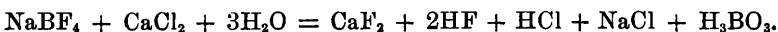
With ethylene no action could be obtained, and the author believes that Landolph's supposed compound was probably the compound  $\text{BF}_3\cdot\text{OEt}_2$ , formed from impurities in the reacting substances.

Acetone absorbs boron fluoride readily, but only the same ethylic compounds described above are formed. Landolph's formulæ are incorrect. If heat is used, however, the boron fluoride acts as a dehydrating agent, and mesityl oxide, mesitylene, phorone, pentallylene,  $(\text{C}_3\text{H}_4)_5$ , and other unsaturated compounds are formed.

With amylene, boron fluoride causes polymerisation to di- and tri-amylene, but forms no compounds. Benzene is without action on boron fluoride. Cetylic alcohol, glycol, and glycerol act on boron fluoride, but the products could not be isolated. Phenol and thymol have no action. Resorcinol absorbs boron fluoride, and is condensed to diresorcinol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , but no boron or fluorine compound is formed. Boron fluoride thus acts as a strong dehydrating agent.

*Analytical Methods.*—Modifications of the usual methods had to be employed. In determining the hydrogen and carbon by combustion, hydrogen fluoride passes forward, and vitiates the analysis if only copper oxide, lead chromate, or a mixture of these is used. This may be obviated by interposing in the length of mixed oxide and chromate several small plugs or screens of lead peroxide, which retain the fluorine. The combustion must be carried out at the lowest possible temperature, or the tube will be much acted on by the fluorine.

For determining the boron and fluorine in those compounds which are decomposed by water with formation of boric and hydrofluoric acids, the authors employed titration. If "orange Poissier No. 3" or Congo red is used, the indication is given as soon as all the hydrofluoric acid is neutralised, boric acid not affecting these indicators. If now "blue C4B" is used, the indication is given when, in addition to neutralising the hydrofluoric acid, the alkali has been added to the extent of *one* molecule of alkali to each  $\text{B}(\text{OH})_3$ . The reaction is not quite as sharp with mixtures of hydrofluoric and boric acids as with those with hydrochloric and boric acids, but is still very serviceable. For gravimetric determinations, calcium fluoride and calcium or magnesium borate are the best compounds to employ. It is necessary to keep the solutions neutral in the precipitation of calcium fluoride, as otherwise the precipitation is not complete, and where the substance is originally present as a borofluoride, acid is liberated during the formation of the calcium fluoride. This is due to the action expressed by the following equation



The filtrate from the fluoride is treated with ammonium oxalate to precipitate the lime, and the filtrate from this (containing all the boric acid as ammonium borate, together with ammonium chloride or nitrate and oxalate) evaporated in a platinum crucible containing a known weight of pure and ignited lime, or, preferably, magnesia.

This is then gradually heated to expel the ammonium salts, and finally strongly ignited, when the excess over the previous weight represents the boric acid.

Ditte's method of fusing a fluoborate with calcium chloride in the presence of a molecular mixture of potassium and sodium chlorides also gives very good results. In the melt, the fluorine is in the form of calcium fluoride, and the boric acid as the crystalline and insoluble calcium borate. The alkali chlorides are removed by washing, the mixed fluoride and borate weighed, the borate then dissolved out by a hot concentrated solution of ammonium nitrate, and the fluoride re-weighed. The boric acid determination is slightly too low, owing to a trace of the calcium borate being dissolved out with the alkali chlorides. L. T. T.

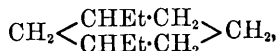
**Molecular Change Produced in Allofurfuracrylic acid and Allocinnamylideneacetic acid by Exposure to Sunlight.** By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1443—1448; compare *Abstr.*, 1894, i, 173, and this vol., i, 470).—Allofurfuracrylic acid is slowly converted into the ordinary acid when its solution in benzene is exposed to sunlight, but the change occurs after only about half an hour's exposure when a little iodine is added, although the solution containing iodine is quite unaltered in the dark. The analogous change is particularly rapid and striking in the case of allocinnamylideneacetic acid. The conversion of allocinnamic acid into its stereoisomeride is also facilitated by the addition of iodine to the solution, but still requires an exposure extending over several days. The action of the iodine is probably a purely chemical one. A. H.

**Isomerides of Hexanaphthene (Cyclohexane).** By F. MARKOVNIKOFF and MICHAËL KONOVALOFF (*Ber.*, 1895, **28**, 1234—1237; compare this vol., i, 271).—A fraction of Caucasian naphtha, free from aromatic compounds, boiling at 70°, and having sp. gr. = 0.710 at 15°, was nitrated and treated with potash. The portion insoluble in alkali boiled at 179—181°, and had sp. gr. = 1.0011 at 20°/0°; the results of analyses agreed with the formula  $C_6H_{11}NO_2$ . An amine was obtained on reduction, boiling at 114°, and having sp. gr. = 0.8367 at 0°/0° and 0.8197 at 20°/0°. The hydrochloride crystallises from hot water in small needles, and melts and decomposes at 228°; the platinochloride crystallises in highly refractive, orange-yellow octahedra and tetrahedra. The aurochloride crystallises in long, slender, orange-red needles.

Chlorine converts the hydrocarbon into a chloro-derivative of the formula  $C_6H_{11}Cl$ ; it is probable that the nitro-compound has the constitution  $\begin{array}{c} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{array} > CMe \cdot NO_2$ . M. O. F.

**1.3-Diethylhexamethylene.** By NICOLAI D. ZELINSKY and W. RUDEWITSCH (*Ber.*, 1895, **28**, 1341—1344).—Crude diethylpimelic acid, prepared by the action of trimethylenic bromide on ethylic sodiocyanobutyrate, on distillation in a vacuum yields a colourless oil, which boils at 205—207°, and is probably diethylketohexamethylene,

$\text{CO} < \begin{smallmatrix} \text{CHEt} \cdot \text{CH}_2 \\ \text{CHEt} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ . This substance is converted by reduction into the alcohol,  $\text{OH} \cdot \text{CH} < \begin{smallmatrix} \text{CHEt} \cdot \text{CH}_2 \\ \text{CHEt} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ , which boils at  $209-211^\circ$ , and partially solidifies on standing, the crystalline portion melting at  $77-78^\circ$ . When this alcohol is converted into the iodide, and the latter reduced by means of zinc and hydrochloric acid in alcoholic solution, the product consists of *diethylhexamethylene*,



which is a colourless liquid with an odour resembling that of petroleum. It boils at  $169-171^\circ$ , and has sp. gr. =  $0.7957$  at  $22^\circ/0^\circ$ , and the refractive index  $1.4388$  at  $20^\circ$ , whence the molecular refraction is found to be  $46.13$ . This agrees with the calculated number for a saturated hydrocarbon of the same formula, and the saturated character of the compound is also shown by the fact that it is immediately coloured by bromine vapour.

A. H.

**Phenylnitromethane.** By ARNOLD F. HOLLEMANN (*Rec. Trav. Chim.*, 1894, **13**, 403—410).—Phenylnitromethane,  $\text{CH}_2\text{Ph} \cdot \text{NO}_2$ , is formed by the action of silver nitrite on benzylic chloride, as may be proved by reducing the product with zinc dust and dilute sulphuric acid, and isolating the benzylamine thus formed as its benzoyl-derivative. (Benzylbenzamide melts at  $98^\circ$ , and not at  $105-106^\circ$ , as stated by Beckmann.) Benzylic nitrite is also formed, as benzylic alcohol is present in the reduction product.

Previous attempts to isolate the nitro-compound by distillation have failed, owing to its instability even at moderate temperatures, but it may be readily isolated by means of its insoluble sodium derivative; the crude nitro-compound, obtained by extracting the product with ether, is treated with a solution of sodium methoxide in methylic alcohol, and the sodium derivative washed with benzene, and decomposed by the calculated quantity of acetic acid; the nitro-compound is then extracted with ether and purified by distillation, first with steam, and subsequently under low pressure in an atmosphere of carbonic anhydride.

*Phenylnitromethane* is a pale yellow, heavy oil, having an odour resembling that of nitrobenzene. It boils at  $158-160^\circ$  ( $35$  mm.), and even at that temperature decomposes slightly; when heated under ordinary pressure, it decomposes entirely at a temperature far below that at which it is stated by Gabriel (*Ber.*, **27**, 2738) to boil.

*Benzeneazophenylnitromethane*,  $\text{NPh} : \text{N} \cdot \text{CHPh} \cdot \text{NO}_2$ , prepared by the action of diazobenzene nitrate on the pure or crude nitro-compound for purposes of characterisation, crystallises from alcohol in vermilion plates, and melts and decomposes at  $101^\circ$ . It forms dark, yellowish-red solutions in alkalis, from which it is reprecipitated by acids, and it dissolves in concentrated sulphuric acid to an intensely blue solution.

*Benzylic nitrite*, which is the principal product in the preparation

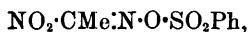
of the nitro-compound, is a liquid, the vapour of which attacks the eyes; it boils at 136—138° (35 mm.). JN. W.

**Action of Nitrous acid on Cinnamene.** By E. A. SOMMER (*Ber.*, 1895, **28**, 1328—1331).—When nitrous acid is passed into an ethereal solution of cinnamene obtained from coal gas (compare Priebis, *Abstr.*, 1885, 160), the crystals, formed in addition to phenyl-nitroethylene, which melt at 158°, are shown to be the  $\alpha$ -nitrosite,  $C_8H_8N_2O_3$ ; crystals melting at 105°, and yellow crystals, perhaps identical, but melting some at 232°, some at 215°, are also obtained. When a saturated solution of potassium nitrite is allowed to act on an acetic acid solution of cinnamene, there are obtained, besides the  $\alpha$ -nitrosite, greenish needles, melting at 103·5°, of a compound,  $C_8H_8N_3O_4$ , possibly a nitro-derivative of the peroxide; yellowish crystals melting at 123°, and crystals melting at 200°. White crystals melting at 130° are obtained when strong nitric acid acts on a mixture of cinnamene, amylic nitrite, and acetic acid. C. F. B.

**Halogen Derivatives of Catechol.** By H. COUSIN (*Compt. rend.*, 1895, **120**, 840—842).—*Trichlorocatechol*,  $C_6H_3Cl_3O_2$ , is obtained by the action of the calculated quantity of chlorine, dissolved in acetic acid, on a solution of catechol in a mixture of acetic acid and chloroform. It crystallises from hot, dilute acetic acid in colourless, odourless prisms, with a burning taste. The crystals melt at 104—105°, and contain 1 mol.  $H_2O$ , half of which is given off in a dry vacuum, and the resulting hydrate melts at 134—135°. *Trichlorocatechol* is insoluble in cold water, very soluble in alcohol, ether, acetic acid, &c., Excess of chlorine converts it into tetrachlorocatechol.

*Dibromocatechol*,  $C_6H_4Br_2O_2$ , is obtained by the action of the calculated quantity of bromine on catechol in presence of acetic acid. It crystallises from hot, dilute acetic acid in large prisms, melts at 92—93°, and is insoluble in water, but soluble in ordinary organic solvents. Excess of bromine converts it into tetrabromocatechol, and when heated with sulphuric acid at about 80°, it also yields the tetrabromo-derivative and resinous products. Chlorine converts it into the tetrachloro-compound. C. H. B.

**Nitrolic acids.** By ALFRED WERNER and HANS BUSS (*Ber.*, 1895, **28**, 1280—1282).—It has been found impossible to isolate alkyl ethers of the nitrolic acids, whilst acid derivatives can readily be obtained pure. *Benzoylamylnitrolic acid*,  $CH_3 \cdot [CH_2]_3 \cdot C(NO_2) \cdot NOBz$ , is formed when an alkaline solution of amylnitrolic acid is shaken with benzoic chloride. It crystallises in prisms, melts at 83°, and is very stable. The *benzenesulphonic ether of ethylnitrolic acid*,



may be prepared from ethylnitrolic acid by the action of benzenesulphonic chloride. It crystallises in cubes melting at 90—91°.

When ethylnitrolic acid is treated in ethereal solution with hydrogen chloride, a white substance is formed, which melts at 141°, and

deliquesces and decomposes in the air. This compound is probably a *hydrochloride* of the formula  $\text{CMeCl.NOH.HCl}$ . A. H.

**Acid Benzylamine Oxalate.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1894, **13**, 411—416).—In characterising benzylamine in presence of ammonia (this vol., i, 455), the platinum method did not give satisfactory results, as the platinochloride could not be completely separated from ammonium platinochloride. The benzylamine was therefore isolated as the acid oxalate. This, when prepared from pure materials, forms large, prismatic crystals with  $\text{1H}_2\text{O}$ , half of which it loses at  $106^\circ$ , and the remainder at  $150^\circ$ . It melts at  $175^\circ$ , at the same time decomposing into dibenzylloxamide *benzylammonium benzyloxamate*,  $\text{CH}_2\text{Ph.NH.CO.COONH}_2\text{CH}_2\text{Ph}$ , and *formylbenzylamine (benzylformamide)*. The last melts at  $49^\circ$ , and is easily soluble in alcohol and ether.

Acid ethylamine oxalate undergoes a similar decomposition into diethylloxamide and ethylformamide. JN. W.

**Paradiamidobenzylic Sulphide.** By OTTO FISCHER (*Ber.*, 1895, **28**, 1337—1341; compare this vol., i, 343).—*Paradinitrobenzylic sulphide* is formed by the action of alcoholic ammonium sulphide on *paranitrobenzylic chloride*, although the product of this reaction has been described by Strakosch (*Ber.*, **5**, 698) as *paranitrobenzylic hydrosulphide*. It crystallises in lustrous plates melting at  $159^\circ$ . On reduction with stannous chloride and hydrochloric acid, it is converted into *diamidobenzylic sulphide*, identical in every respect with that previously prepared from *benzylic acetate*. A number of condensation products of the *diamidobenzylic sulphide* have been prepared. The *orthohydroxybenzylidene* compound melts at  $176$ — $177^\circ$ . The corresponding *cinnamylidene* compound melts at  $158$ — $159^\circ$ , and not at  $155^\circ$ , as previously stated. The *paranitrobenzylidene compound* forms yellow needles melting at  $173^\circ$ . The *thiocarbamide* is a yellowish-white, crystalline powder, scarcely soluble in the usual solvents, which melts above  $220^\circ$ , and is insoluble in alkalis. The *phthalide* of *diamidobenzylic sulphide* crystallises in large, yellowish needles, and melts at  $225^\circ$ . *Paradibenzyl sulphide tetrazo- $\alpha$ -naphthol* forms small, dark red crystals, and melts and decomposes at  $198^\circ$ . The corresponding  *$\beta$ -naphthol compound* forms red plates melting at  $237^\circ$ , whilst the *resorcinol derivative* is a brown, crystalline powder, which melts and decomposes at  $211^\circ$ .

*Paradiamidobenzylic sulphide* gives a precipitate of silver sulphide with solutions of silver salts, and also readily loses sulphur on reduction, paratoluidine being formed. It also readily reacts with aniline at  $150$ — $160^\circ$  in presence of zinc chloride, *diamidodiphenylmethane* being formed. A. H.

**Conversion of Symmetrical Triamidophenol into 1:2:3:5-Tetrahydroxybenzene (Phentetrol).** By KARL OETTINGER (*Monatsh.*, 1895, **16**, 248—259).—When symmetrical triamidophenol hydrochloride, in dilute solution, is heated during four to five hours, it is decomposed into ammonium chloride and trihydroxyamido-benzene hydrochloride. During this operation, it is necessary to pass

a slow stream of hydrogen through the liquid in order to prevent oxidation. The solution is then evaporated to dryness under diminished pressure and at a low temperature, and the residue is treated with acetic anhydride in order to separate the ammonium chloride from the trihydroxyamidobenzene hydrochloride. This latter compound is converted into a mixture of its tri- and tetra-acetyl derivatives, which can be distilled under reduced pressure, and subsequently separated by repeated recrystallisation from benzene.

*Tetracetyltrihydroxyamidobenzene*,  $C_6H_2(OAc)_3 \cdot NHAc$ , forms a colourless powder which consists of minute, glistening crystals. It is sparingly soluble in water, but readily dissolves in hot alcohol and benzene, and melts at  $182^\circ$  (uncorr.).

The *triacetyl* derivative,  $C_6H_2(OAc)_3 \cdot NH_2$ , is sparingly soluble in benzene, but readily in warm water and in alcohol. It forms colourless needles, which melt at  $182-184^\circ$  (uncorr.). Both compounds when heated with hydrochloric acid at  $100^\circ$  are hydrolysed into *trihydroxyamidobenzene hydrochloride* and acetic acid. The hydrochloride forms small, colourless crystals, which are readily soluble in water and in alcohol. The aqueous solution turns brown on exposure to the air, gives a deep red coloration with ferric chloride, and a green colour with alkalis.

*1:2:3:5-Tetrahydroxybenzene* is obtained when the pure trihydroxyamidobenzene hydrochloride is heated with excess of water at  $150-160^\circ$  during eight hours. The operation is best carried out in an autoclave, in which the air has been replaced by hydrogen. The phenetrol forms colourless crystals, which melt in a vacuum at  $165^\circ$  (uncorr.). It is readily soluble in water, alcohol, and ethylic acetate, but is insoluble in benzene, light petroleum, and chloroform. The aqueous solution gives a light yellow precipitate with lead acetate, and a red coloration with ferric chloride. With concentrated alkali, the phenetrol gives a dirty green colour, which changes to a violet-blue on dilution.

J. J. S.

**Acetyl Derivatives of Symmetrical Triamidophenol.** By KARL OETTINGER (*Monatsh.*, 1895, 16, 260-265).—Bamberger (*Abstr.*, 1884, 309) states that when dry triamidophenol hydrochloride is heated with acetic anhydride and sodium acetate, a triacetyl derivative is obtained. The author finds that the chief product of the action of acetic anhydride on the hydrochloride is a hexacetyl derivative, together with smaller quantities of the tetra- and tri-acetyl compounds.

*Hexacetyltriamidophenol*,  $OAc \cdot C_6H_2(NAc)_2 \cdot NHAc$ , is readily soluble in warm water, alcohol and acetic acid. After recrystallisation from alcohol, it forms small, glistening, prismatic crystals, which melt at  $184^\circ$ . It is slowly decomposed by dilute alkalis, and the triacetyl compound described by Bamberger is formed.

The tetra- and tri-acetyl derivatives are best separated by fractional crystallisation from water.

*Triacetyltriamidophenol*,  $OH \cdot C_6H_2 \cdot (NHAc)_3$ , forms small, colourless crystals, which melt at  $279^\circ$  (uncorr.). It is readily soluble in hot water and in alcohol, sparingly in ether and benzene. It dissolves in dilute alkalis, from which it is precipitated unaltered by acetic acid.



*Tetracetyltriamidophenol*,  $\text{OAc}\cdot\text{C}_6\text{H}_2(\text{NHAc})_3$ , forms very minute, prismatic crystals, which melt at  $255^\circ$  (uncorr.). It is much more readily soluble in water and alcohol than the triacetyl compound. It dissolves in dilute alkalis, but on the addition of acetic acid the triacetyl derivative of melting point  $279^\circ$  is thrown down.

J. J. S.

**Constitution of Isodiazohydrates.** By EUGEN BAMBERGER (*Ber.*, 1895, 28, 1218—1222; compare this vol., i, 274).—Evidence supporting the author's views regarding the constitution of isodiazohydrates (*loc. cit.*) is afforded by the observation that these substances are formed when hydroxylamine acts on nitroso-compounds; they are, therefore, oximes of nitroso-compounds, and thus differ structurally from the normal diazo-hydrates, which are not formed in this way. Experimental details of the conversion of nitrosobenzene, parabromonitrosobenzene, and paranitrosotoluene into isodiazobenzene, parabromisodiazobenzene, and paraisodiazotoluene respectively, are to be found in the original paper.

*Parabromophenylhydroxylamine*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{OH}$  [1 : 4], crystallises in silvery, nacreous plates, and melts at  $91\text{--}92^\circ$ ; the *nitrosamine*, obtained by the action of nitrous acid, melts at  $87^\circ$ .

*Parabromonitrosobenzene*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}$ , is obtained by oxidising parabromophenylhydroxylamine with ferric chloride; it crystallises in colourless needles, and melts at  $92\text{--}92.5^\circ$ , forming a grass-green liquid. This colour also characterises the solutions of the compound, which resembles the nitroso-compounds already described in regard to odour and volatility.

When parabromonitrosobenzene is treated with hydroxylamine and  $\beta$ -naphthol, it yields the compound obtained from parabromodiazobenzene and  $\beta$ -naphthol; it crystallises in lustrous, scarlet needles, and melts at  $172\text{--}173^\circ$ .

M. O. F.

**Asymmetrical Ethylic Phenylhydrazidoacetate and its Conversion into Triazine Derivatives.** By CARL D. HARRIES (*Ber.*, 1895, 28, 1223—1230; compare the following abstract).—When the nitroso-derivative of ethylic phenylamidoacetate is reduced, ethylic phenylhydrazidoacetate is formed; it differs completely from the isomeric substance obtained by Reissert and Kayser from ethylic chloracetate and phenylhydrazine, and as, from its mode of formation, the new compound is undoubtedly asymmetrical in structure, it follows that the isomeride must be regarded as the symmetrical compound,  $\text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOEt}$ .

*Ethylic nitrosophenylamidoacetate*,  $\text{NO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{COOEt}$ , is a viscous, reddish-yellow oil, obtained by the action of nitrous acid on ethylic phenylamidoacetate; it is insoluble in water and alkalis and gives Liebermann's reaction.

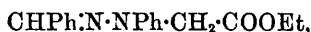
*Asymmetrical ethylic phenylhydrazidoacetate*,  $\text{NH}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{COOEt}$ , is obtained by reducing the alcoholic solution of the foregoing compound with zinc dust and glacial acetic acid; it is a slightly coloured oil, which boils at  $157\text{--}161^\circ$ , under a pressure of 7 mm. It reduces platinum tetrachloride and silver nitrate in the cold, and Fehling's

solution when gently heated. The *hydrochloride* crystallises in long white needles; it melts and decomposes at 195—196°. The *nitrate* melts at 143—144°, and the *sulphate* crystallises in leaflets.

*Asymmetrical phenylhydrazidoacetic acid* is easily prepared from the ethylic salt; it crystallises from hot alcohol in lustrous, white, six-sided tablets, and melts at 167° with evolution of gas. It reduces Fehling's solution, and dissolves in nitric acid with development of a red coloration; the *hydrochloride* crystallises in long needles.

*Diethylic diphenyltetrazonediacetate*,  $N_2(NPh \cdot CH_2 \cdot COOEt)_2$ , is obtained by the oxidation of asymmetrical phenylhydrazidoacetate with mercuric oxide; it crystallises from alcohol in needles, and melts at 117°. It is indifferent towards Fehling's solution and is decomposed by fuming hydrochloric acid, gas being evolved.

*Ethylic benzylidenephénylhydrazidoacetate*,



is obtained from ethylic phenylhydrazidoacetate and benzaldehyde; it crystallises from ether in white, six-sided plates, sinters at 70°, and melts at 73—74°.

The compound,  $NHPh \cdot CS \cdot NH \cdot NPh \cdot CH_2 \cdot COOEt$ , is obtained from ethylic phenylhydrazidoacetate and phenylthiocarbimide; it crystallises from amyl alcohol in short prisms, and melts at 155—156°.

When ethylic phenylhydrazidoacetate is heated with formamide (1 mol.) for four hours at 130°, it is converted into *hydroxyphenyldihydrotriazine*,  $NPh \cdot \left\langle \begin{array}{c} CH_2 \cdot C(OH) \\ N = C \end{array} \right\rangle N$ , which crystallises in lustrous, yellowish-green plates, and decomposes at 203—204°; it dissolves in alkalis, and is decomposed when boiled for a considerable time with aqueous potash. The compound is indifferent towards Fehling's solution, and is soluble in concentrated nitric acid with development of a brownish-red coloration.

*Methylphenyltetrahydroketotriazine*,  $NPh \cdot \left\langle \begin{array}{c} CH_2 \cdot CO \\ N = CH \end{array} \right\rangle NMe$ , is obtained by methylating the foregoing compound, or by heating a mixture of methylformamide and ethylic phenylhydrazidoacetate for four hours at 135°. It crystallises in lustrous, white leaflets and melts at 179—180°.

*Diphenyltetrahydroketotriazine*,  $NPh \cdot \left\langle \begin{array}{c} CH_2 \cdot CO \\ N = CH \end{array} \right\rangle NPh$  (compare Abstr., 1894, i, 57) is formed when formanilide and ethylic phenylhydrazidoacetate in molecular proportion are heated with alcohol at 150—160°; it crystallises in long, slender, needles, and melts at 204—205°. It closely resembles Widman's compound (*loc. cit.*), with which it is isomeric.

M. O. F.

**Action of Ethylic Chloracetate on Phenylhydrazine.** By ARNOLD REISSERT (*Ber.*, 1895, 28, 1230—1234; compare Reissert and Kayser, Abstr., 1891, 1054).—The wide difference in properties exhibited by asymmetrical ethylic phenylhydrazidoacetate (preceding abstract) and the product obtained from ethylic chloracetate and phenylhydrazine, has led the author to reinvestigate this substance, and it

is now found that symmetrical ethylic phenylhydrazidoacetate is the product of the reaction; a certain amount of the hydrazone of ethylic glyoxylate is also formed, arising from oxidation of the chief product.

The *phenylhydrazone* of ethylic glyoxylate,  $\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{COOEt}$ , crystallises in white needles, and melts at  $129^\circ$ ; it is feebly basic, and is oxidised when heated for a considerable time with Fehling's solution. It is readily hydrolysed with aqueous soda, yielding the *phenylhydrazone* of glyoxylic acid, which separates from ethylic acetate in yellowish crystals and melts at  $138^\circ$ .

Symmetrical phenylhydrazidoacetic acid has been described by Elbers (Abstr., 1885, 535). The *ethylic* salt,  $\text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOEt}$ , is a yellow oil which solidifies at a low temperature and reduces Fehling's solution; the *hydrochloride* crystallises in snow-white needles and melts at  $190$ — $191^\circ$ . M. O. F.

**Benzyl Ethers of Oximes.** By ALFRED WERNER and HANS BUSS (Ber., 1895, 28, 1278—1280).—When the  $\alpha$ -benzyl ether of benzaldoxime is heated with hydrochloric acid, only a very small amount of  $\alpha$ -benzylhydroxylamine is produced. The chief product of the reaction is a solid substance, which crystallises from alcohol in slender needles, melts at  $29^\circ$ , and is probably a benzyl-ether of benzaldoxime,  $\text{CHPh}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ .

When acetoxime is treated in alcoholic solution with sodium ethoxide and benzylic chloride, the nitrogen ether,  $\text{CMe}_2\text{<}\overset{\text{O}}{\text{N}}\cdot\text{CH}_2\text{Ph}$ , (Beckmann, Abstr., 1889, 607), is formed in addition to the oxygen-ether which is the chief product. This substance is also formed when acetoxime is converted into the benzyl derivative by the method of Japp and Klingemann (Beckmann, Abstr., 1889, 607).

A. H.

**Modification of the Baumann-Schotten Method.** By ALBERT DENINGER (Ber., 1895, 28, 1322).—The substance is dissolved in pyridine, the acid chloride slowly added, and the whole then poured into water. In this way *diphenylthiocarbamide* yielded a yellowish *monacetyl* and a yellow *dibenzoyl derivative*; these melt respectively at  $91^\circ$  and  $160\cdot5^\circ$ . C. F. B.

**Benzylic Chloride as a Desulphurising Agent. Derivatives of Cyanamide.** By EMIL FROMM (Ber., 1895, 28, 1302—1308).—Benzylic chloride in presence of alkali very readily yields substituted benzylic derivatives with sulphur compounds, such as the keturet of phenyldithiobiuret,  $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{N}\text{<}\overset{\text{C}\cdot\text{SH}}{\text{CMe}_2}\text{>N}$ , (Abstr., 1893, i, 575). When, however, phenyldithiobiuret itself is treated with benzylic chloride and an alkali, a further action goes on, *phenyl- $\psi$ -benzylcyanothiocarbamide*,  $\text{NPh}\cdot\text{C}(\text{SC}_7\text{H}_7)\cdot\text{NH}\cdot\text{C}\cdot\text{N}$ , which melts at  $190^\circ$ , being formed, along with benzylic sulphide. It is probable that in this reaction sodium sulphide is first produced and then reacts with the benzylic chloride, the sulphur being removed from the solution in the form of insoluble benzylic sulphide. The phenylbenzyl-

cyanothiocarbamide when boiled with hydrochloric acid yields aniline and *benzylic thioallophanate*, which melts at 179—180°. The latter is decomposed by ammonia with formation of benzylic hydrosulphide and biuret.

A similar reaction occurs when phenylthiocarbamide is treated with alcoholic soda and benzylic chloride, the whole of the sulphur being removed in the form of benzylic sulphide and phenylcyanamide formed. *Benzoylphenylcyanamide* crystallises from alcohol in needles and melts at 118°. Diphenylthiocarbamide is desulphurised in the same manner, but the insoluble carbodiphenylimide which is first formed readily takes up the elements of water forming diphenylcarbamide.

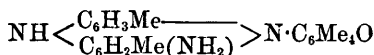
Methylphenyldithio-*c*-methylalduret (this vol., i, 418), which is obtained by the action of acetaldehyde on methylphenyldithiobiuret, also undergoes partial desulphurisation in the presence of alcoholic soda and benzylic chloride, *methylphenylcyanothiocarbamide*,



being produced. This substance crystallises in needles, melts at 210°, and is insoluble in alkalis.

A. H.

**Constitution of the Safranines.** By RUDOLF NIETZKI (*Ber.*, 1895, 28, 1354—1357).—The conclusion that the safranines have a symmetrical constitution which has been arrived at by Jaubert (this vol., i, 278) is not justified, because a substance of asymmetrical formula might just as easily be obtained by the oxidation of the mixture of metamidodiphenylamines with paradiamines. In order to decide the question, the author attempted to prepare a safranine by oxidising a mixture of diamidodurene, the constitution of which only admits of the formation of an asymmetric derivative, with metamidoditoylamine. A colouring matter is formed by the reaction which, however, is not a true safranine but a safraninone and has the formula,



[NH:Me:N = 1:4:6; NH:NH<sub>2</sub>:Me:N = 1:3:4:6; N:O = 1:4]. The *nitrate*, which is only slightly soluble in water, has the formula, C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O, HNO<sub>3</sub> +  $\frac{1}{2}$ H<sub>2</sub>O. The existence of an asymmetrical compound so closely related to the safranines renders it at least possible that the compounds of the latter class may also have the asymmetrical constitution. The nature of the colouring matter obtained is being further investigated. The author has found that the compound prepared from dimethylparaphenylenediamine and aniline is different from that obtained from paraphenylenediamine and dimethylaniline. The latter product, however, appears to be a monomethylsafranine, although prepared by the aid of pure dimethylaniline.

The reaction is therefore being again examined.

A. H.

**Thiophosphazo-compounds.** By C. A. AUGUST MICHAELIS and W. KÄRSTEN (*Ber.*, 1895, 28, 1237—1246).—The action of phosphorus thiochloride on aromatic hydrochlorides is different to that of phosphorus oxychloride; compounds of the general formula RN:PSCl

are formed corresponding with phosphazobenzene chloride,  $\text{PhN:PCl}_2$ , prepared from phosphorus trichloride and aniline hydrochloride; no derivatives similar to the *n*-oxychlorophosphines could be isolated.

*Thiophosphazobenzene chloride*,  $\text{NPh:PSCl}_2$ , prepared by the prolonged heating of aniline hydrochloride and phosphorus thiochloride, is deposited in large, colourless, monoclinic crystals containing  $\frac{1}{2}$  mol. benzene; when dry it melts at  $149^\circ$ , boils at  $280\text{--}290^\circ$  (80 mm.), and is stable towards water, alkalis, and acids. By heating with concentrated hydrochloric acid at  $150^\circ$ , it is resolved into aniline hydrochloride, hydrogen sulphide, and phosphoric acid. The *ethoxy*-derivative,  $\text{NPh:PS}\cdot\text{OEt}$ , formed by the action of sodium ethoxide on the preceding compound, is deposited in colourless crystals, melts at  $206^\circ$ , and is extremely stable. The *anilide*,  $\text{NPh:PS}\cdot\text{NHPh}$ , is obtained by heating phosphorus thiochloride (2 mols.) and aniline hydrochloride (1 mol.) at  $130\text{--}140^\circ$ , and also by the action of aniline on the above chloride; it crystallises in slender, colourless needles, melts at  $226\text{--}227^\circ$ , and is decomposed by prolonged boiling with soda.

*Thiophosphazoparachlorobenzene chloride*,  $\text{C}_6\text{H}_4\text{Cl:N:PSCl}_2$ , prepared in a similar manner to the benzene-derivative, is deposited in colourless, compact, monoclinic crystals, melts at  $188^\circ$ , boils at  $230^\circ$  (16 mm.), and is extremely stable. The *ethoxy*-derivative,  $\text{C}_6\text{H}_4\text{Cl:N:PS}\cdot\text{OEt}$ , is deposited from alcohol in large, colourless, well developed, monoclinic crystals, melts at  $91^\circ$ , and is not decomposed by dilute soda.

*Thiophosphazo-orthotoluene chloride*,  $\text{C}_6\text{H}_4\text{Me:N:PSCl}_2$ , obtained from orthotoluidine hydrochloride and phosphorus thiochloride, is deposited from dilute benzene solutions in slender, transparent needles; from concentrated solution, in well developed, transparent, monoclinic crystals; it melts at  $260^\circ$ , boils at  $290^\circ$  (28 mm.), and is not decomposed by boiling alkalis or acids; it is resolved into toluidine hydrochloride, hydrogen sulphide, and phosphoric acid, when heated at  $150^\circ$  with concentrated hydrochloric acid. The yield is 65 per cent. of the theoretical. The *ethoxy*-derivative,  $\text{C}_6\text{H}_4\text{Me:N:PS}\cdot\text{OEt}$ , crystallises in slender, colourless, stellate needles melting at  $176^\circ$ . The *phenoxy*-derivative,  $\text{C}_6\text{H}_4\text{Me:N:PS}\cdot\text{OPh}$ , is colourless, crystalline, melts at  $236^\circ$ , and is not decomposed by heating with dilute acids or alkalis. The *paratolylloxy*-derivative,  $\text{C}_6\text{H}_4\text{Me:N:PS}\cdot\text{OC}_6\text{H}_5$ , is crystalline, and melts at  $247^\circ$ . The *piperidide*,  $\text{C}_6\text{H}_4\text{Me:N:PS}\cdot\text{NC}_5\text{H}_{10}$ , prepared from piperidine and the chloride, is colourless, pulverulent, melts at  $236^\circ$ , and is decomposed by soda, but not by dilute acids. The *anilide*,  $\text{C}_6\text{H}_4\text{Me:N:PS}\cdot\text{NHPh}$ , melts at  $162^\circ$ , is colourless and pulverulent. The *orthotoluidide* resembles the anilide, and melts at  $258^\circ$ .

*Thiophosphazoparatoluene chloride* is prepared in a similar manner to the ortho-compound (see above) which it resembles; it crystallises in small, flat, monoclinic prisms, melts at  $170^\circ$ , and decomposes when distilled, even under reduced pressure. The *ethoxy*-derivative is deposited in colourless, feathery crystals, and melts at  $176^\circ$ . The *paratoluidide* is yellow, pulverulent, and melts at  $182^\circ$ . The *piperidide* crystallises from benzene, and melts at  $275^\circ$ .

*Thiophosphazotrimethylbenzene chloride*,  $\text{C}_6\text{H}_2\text{Me}_3\text{N:PSCl}_2$  [ $\text{Me}_3 = 1:2:4$ ], prepared from pseudocumidine hydrochloride and phos-

phorus thiocloride, crystallises in colourless needles, melts at  $257^{\circ}$ , and decomposes when distilled. The *ethoxy*-derivative is deposited in slender needles melting at  $201^{\circ}$ .

The molecular weights of the preceding compounds could not be determined on account of their sparing solubility at low temperatures; it is possible, therefore, that they are greater than the above formulæ indicate; in this case the latter would need revision, and the benzene chloride, for example, might perhaps have the formula  $\text{NPh} < \begin{smallmatrix} \text{P}(\text{SCl}) \\ \text{P}(\text{SCl}) \end{smallmatrix} > \text{NPh}$ .

J. B. T.

**Addition of Hydrocyanic acid to Benzaldehyde.** By CARL GLÜCKSMANN (*Chem. Centr.*, 1894, ii, 663; from *Pharm. Post*, **27**, 389).—In very dilute solution, hydrocyanic acid acts on benzaldehyde only to a very slight extent, and very slowly.

C. F. B.

**Piperic Aldehyde.** By MAX SCHOLTZ (*Ber.*, 1895, **28**, 1368—1369).—*Piperic aldehyde*,  $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} : \text{CH} : \text{CH} : \text{CHO}$ , is formed when piperonylacraldehyde is treated with aldehyde in alkaline alcoholic solution. It crystallises from alcohol in red plates melting at  $89$ — $90^{\circ}$ , and, like piperic acid, gives a blood-red coloration with sulphuric acid. The *phenylhydrazone* crystallises from acetic acid in red needles, and melts at  $190$ — $192^{\circ}$ .

A. H.

**Action of Chloracetone on Sodium Phenoxide and Synthesis of Cumarone Derivatives.** By RICH. STOERMER (*Ber.*, 1895, **28**, 1253—1254).—*Phenoxyacetone*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{COMe}$ , is prepared by the interaction of sodium phenoxide and chloracetone in anhydrous, phenolic solution. After purification by means of its crystalline *hydrogen sodium sulphite*, it boils at  $229$ — $230^{\circ}$  (uncorr.), has a pleasing smell, and is a colourless oil. The *phenylhydrazone* crystallises in colourless plates with a blue fluorescence, and quickly decomposes in air. The *oxime* is oily. Methylcumarone is formed by the action of concentrated sulphuric acid on phenoxyacetone at low temperatures. *Paratolxyloxyacetone*, prepared in a similar manner to the phenoxy-derivative, is liquid, and boils at about  $240^{\circ}$ .  *$\beta$ -Naphthoxyacetone* melts at  $85^{\circ}$ , and yields a comparatively stable *phenylhydrazone* which melts at  $154^{\circ}$ .

J. B. T.

**Products of the Reduction of Oxalyldiacetophenone.** By PAUL F. SCHMIDT (*Ber.*, 1895, **28**, 1206—1212).—Details of an improved method for the preparation of oxalyldiacetophenone (Brömme and Claisen, *Abstr.*, 1888, 691) are given, by which the yield of this substance is raised from 30 per cent. to 50 per cent.; reduction is effected by suspending the finely-divided substance in benzene or ether to which 20 per cent. hydrochloric acid has been added, and agitating the liquid during the addition of small quantities of zinc dust until the ketone is completely dissolved. In this way a compound is formed which melts at  $79^{\circ}$ , and has the formula  $\text{C}_{18}\text{H}_{16}\text{O}_4$ ; on elimination of  $1\text{H}_2\text{O}$ , two isomeric substances are obtained which melt respectively at  $172$ — $173^{\circ}$  and  $142^{\circ}$ . The latter, on reduction, takes up two

atoms of hydrogen,  $1\text{H}_2\text{O}$  being eliminated, and the product,  $\text{C}_{18}\text{H}_{14}\text{O}_2$ , melts at  $119-120^\circ$ .

The *compound*,  $\text{C}_{18}\text{H}_{16}\text{O}_4$ , which melts at  $79^\circ$ , is produced by the addition of 2 atoms of hydrogen to oxalyldiacetophenone, which has the constitution  $\text{COPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$ ; it is an unstable substance, and the yield obtained by the method indicated is not large. The alcoholic solution develops an intense, dark red coloration with ferric chloride, whilst cupric acetate gives rise to a *copper salt*,  $(\text{C}_{18}\text{H}_{15}\text{O}_4)_2\text{Cu}$ , which crystallises in slender, pale green needles and melts at  $187^\circ$ ; the *copper salt* of oxalyldiacetophenone, on the other hand, is a greenish-yellow, amorphous substance, which has the composition  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{Cu}$ , and does not melt below  $220^\circ$ .

The *dioxime anhydride*,  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ , crystallises in slender, white needles and melts at  $157-158^\circ$ .

On decomposing the copper salt of the foregoing compound (m. p.  $79^\circ$ ) with concentrated hydrochloric acid, or on treating the substance itself with warm alcohol or glacial acetic acid, the *compound*,  $\text{C}_{18}\text{H}_{14}\text{O}_3$ , is formed; this melts at  $142^\circ$ , and the *oxime* crystallises in white needles which melt and decompose at  $185^\circ$ . No coloration is developed with ferric chloride, and the substance does not form a copper salt; oxidation with nitric acid gives rise to benzoic acid. The *isomeride* is obtained by treating the original compound,  $\text{C}_{18}\text{H}_{16}\text{O}_4$ , with a large volume of boiling water; it crystallises from alcohol in small prisms and melts at  $172-173^\circ$ , whilst the *oxime* melts at  $179-180^\circ$ . It does not give rise to a copper salt, and no coloration is developed with ferric chloride.

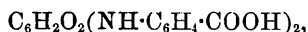
Of these two isomerides, the one melting at  $142^\circ$  yields on reduction with hydriodic acid the *compound*  $\text{C}_{18}\text{H}_{14}\text{O}_2$ , which crystallises from glacial acetic acid in prisms and melts at  $119-120^\circ$ . It is indifferent towards cupric acetate and ferric chloride, and yields benzoic acid on oxidation with nitric acid; the *oxime* melts and decomposes at  $192^\circ$ .

When a solution of oxalyldiacetophenone in glacial acetic acid is boiled with hydriodic acid, a *compound*,  $\text{C}_{18}\text{H}_{16}\text{O}_3$ , is obtained which crystallises in colourless prisms and melts at  $114-115^\circ$ ; it develops a dark red coloration with ferric chloride. The *dioxime anhydride*,  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$ , melts at  $132^\circ$ . The *dibromo-derivative* is obtained by treating the substance dissolved in carbon bisulphide with bromine, which is immediately decolorised; it crystallises from alcohol in yellowish prisms which melt and decompose at  $127^\circ$ . In its unsaturated character the compound melting at  $114-115^\circ$  differs from the foregoing substances, which do not form additive compounds with halogens; it resembles them, however, in its behaviour towards nitric acid, which gives rise to benzoic acid. From consideration of its properties, the formula  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$  appears to express its constitution.

M. O. F.

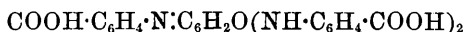
**Action of Amidobenzoic acid on Quinone.** By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1895, 120, 684-685).—When alcoholic solutions of orthoamidobenzoic acid and quinone are mixed,

a purple-red liquid is obtained, which after some time deposits a red-brown, crystalline precipitate of the compound



analogous to the products obtained under like conditions from primary amines of simple function. The two  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$  groups are substituted for  $\text{H}_2$ , and quinol is formed at the same time. The *quinone-bis-orthoamidobenzoic acid* is feebly soluble in alcohol, but insoluble in the other ordinary solvents. It dissolves in sulphuric acid, and forms a blood-red solution, from which it separates unchanged on addition of water. It is a feeble acid, and decomposes carbonates and dissolves readily in alkalis, but is partially precipitated from the latter solutions by a current of carbonic anhydride. When heated, it becomes pasty at about  $325^\circ$ , but decomposes without melting, aniline and benzoic acid being amongst the products of decomposition.

If hot solutions of quinone and orthoamidobenzoic acid in glacial acetic acid are mixed, the liquid has an intense red-brown colour, and a crystalline precipitate separates almost immediately. The mixture is heated on a water bath for about 12 hours, and the precipitate is filtered off and washed with acetic acid. The insoluble product is identical with that obtained in alcoholic solutions. The acid mother liquor, when concentrated, yields the compound



as a black compound, which melts at about  $145^\circ$ , and dissolves readily in alcohol. It is analogous to the compounds obtained by Zincke and Hebebrand from simple amines, and hence it follows that orthoamidobenzoic acid behaves towards quinone in the same way as simple amines, whilst the quinone has some properties in common with the diketones.

C. H. B.

**Etherification of Aromatic acids.** By VICTOR MEYER (*Ber.*, 1895, **28**, 1254—1270; compare *Abstr.*, 1894, i, 243, 463, and this vol., i, 93, 228).—Dibromobenzoic acid [ $\text{COOH}:\text{Br}_2 = 1:2:6$ ] melts at  $146.5^\circ$ , not at  $137^\circ$  as previously stated. Some acids, although apparently pure, give small quantities of ethereal salts when treated in alcoholic solution with hydrogen chloride, but when the operation is repeated no salt is produced; a specimen of mesitylenecarboxylic acid gave at  $0^\circ$ , each time, 3.6 per cent. of ethereal salt; another specimen, after being etherified once, yielded practically none, in other respects the acids were identical; the nature of the impurity in the former specimen has not been determined. Thymotic acid,  $\text{HO}\cdot\text{C}_6\text{H}_2\text{MePr}\cdot\text{COOH}$  [ $\text{COOH}:\text{OH}:\text{Pr}:\text{Me} = 1:2:3:6$ ], phenylhydroxybenzoic acid [ $\text{COOH}:\text{Ph}:\text{OH} = 1:2:6$ ], and naphtholcarboxylic acid [ $\text{COOH}:\text{OH} = 1:2$ ], give no methylic salt by the action of methylic alcohol and hydrogen chloride, but the isomeric naphtholcarboxylic acid [ $\text{COOH}:\text{OH} = 2:3$ ] behaves like benzoic acid. These facts show that diorthosubstituted acids are not etherified at low temperatures when one of the substituting groups is hydroxyl.



In explanation of his results, the author has previously advanced a stereochemical hypothesis, from which the following deductions may be drawn:—

1. Symmetrical trisubstituted carboxylic acids should not be etherified, but those in which the carboxyl group is linked by one or more carbon atoms to the benzene nucleus should readily yield ethereal salts. This has been already shown to be correct in the case of mesityl-acetic acid and mesitylglyoxylic acid; mesitylpropionic acid could not be prepared by means of Perkin's reaction. *Tribromamidophenylpropionic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{HBr}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  [ $\text{CH}_2 : \text{NH}_2 = 1 : 3$ ;  $\text{Br}_3 = 2 : 4 : 6$ ], is prepared from metanitrocinnamic acid; it crystallises in lustrous plates, melts at  $188^\circ$ , and yields 98.8 per cent. of methylic salt. *Tribromophenylpropionic acid*,  $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  [ $\text{CH}_2 : \text{Br}_3 = 1 : 2 : 4 : 6$ ], obtained from the preceding compound, crystallises in slender needles, melts at  $150^\circ$ , and yields about 89 per cent. of methylic (?) salt, which also crystallises in needles melting at  $78^\circ$ . *Trimethyl- $\beta$ -benzoylpropionic acid*,  $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  [ $\text{CO} : \text{Me}_3 = 1 : 2 : 4 : 6$ ], is prepared by the action of aluminium chloride on mesitylene and succinic anhydride in carbon bisulphide solution; it crystallises in needles, melts at  $109^\circ$ , and yields about 89 per cent. of ethereal salt. By the action of hydriodic acid the compound is resolved into mesitylene and succinic acid.

2. Etherification should be diversely influenced by substituting groups or elements of different relative mass. In order to test this deduction, the acids, in boiling methylic alcoholic solution, were treated with hydrogen chloride during five hours. Symmetrical trichloro-, tribromo-, and trinitro-benzoic acids and 2 : 6-dibromobenzoic acid were not etherified; thymotic acid, 2 : 6-hydroxyphenylbenzoic acid, and mesitylenecarboxylic acid gave 23.3, 76.5, and 64.5 per cent. of methylic salt respectively. Tetrachlororthamidobenzoic acid gives 22 per cent. of methylic salt when heated, but none at  $0^\circ$ . It appears, therefore, that those radicles which prevent etherification at high temperatures have a much greater relative mass than those which only hinder it at low temperatures, but it is probable that the methylic group and its normal homologues will produce almost identical effects, since the action is chiefly due to that carbon atom which is directly linked to the benzene nucleus.

3. According to theory, those ethereal salts which are formed with greatest difficulty should be hydrolysed least readily. The acids examined were treated in alcoholic solution with soda, during two hours at  $12^\circ$ . 2 : 1-Chloronaphthalenecarboxylic acid gave no acid, the isomeric acid [ $\text{COOH} : \text{Cl} = 3 : 2$ ] gave about 71 per cent. Similar results were obtained with the corresponding hydroxy-acids.

The velocity of etherification of a number of isomeric substituted benzoic acids has also been determined. The acid (1 gram), dissolved in ethylic alcohol (10 c.c.), was mixed with saturated alcoholic solution of hydrogen chloride (90 c.c.), and treated during five hours with a slow current of hydrogen chloride, the temperature being maintained at about  $20^\circ$ ; the quantity of ethylic salt and of unaltered acid were both determined. Figures given show the percentage of acid etherified. Toluic acids: ortho-, 26; meta-, 59; para-, 41.8.

Bromobenzoic acids: ortho-, 30.5; meta-, 69.6. Nitrobenzoic acids: ortho-, 8.3; meta-, 69.9. The ortho-acids are therefore much more difficult to etherify than the isomeric compounds; this is in accordance with determinations of the velocity of hydrolysis of the two ethylic bromobenzoates, under similar conditions; 69 per cent. of the ortho- and 89 per cent. of the meta-salt is decomposed.

Tricarballic acid and hemimellitic acid are comparable in constitution; at 0°, the former yields a tri-, the latter a di-, ethereal salt, indicating that in the first compound the open chain permits the middle carboxylic group to rotate, whilst in the second, the closed chain prevents this.

J. B. T.

**Condensation Products of Piperonylacraldehyde and Synthetic Piperine Derivatives.** By MAX SCHOLTZ (*Ber.*, 1895, 28, 1187—1197; compare this vol., i, 42).—*α-Methylpiperic acid*,



is obtained by heating a mixture of piperonylacraldehyde with sodium propionate and propionic anhydride for six hours. It melts at 208—209°, and sublimes above this temperature. The acid is readily soluble in alcohol, ether, and acetone, and in hot glacial acetic acid, from which it separates in slender needles; it dissolves sparingly in benzene, and is insoluble in light petroleum and carbon bisulphide. A deep red coloration is developed on dissolving the substance in concentrated sulphuric acid. The *sodium* salt is insoluble in alcohol, and sparingly soluble in cold water. The *barium*, *calcium*, *magnesium*, *cobalt*, *nickel*, and *copper* salts are crystalline, and scarcely soluble in water; the *silver* salt is amorphous.

*α-Ethylpiperic acid* crystallises from alcohol in yellow needles and melts at 179°, subliming when heated above this temperature. Its salts resemble those of methylpiperic acid.

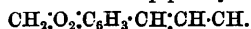
*α-Isopropylpiperic acid* blackens, but does not melt, at 240°. Its salts are similar to those of the foregoing acids, whose behaviour towards solvents it resembles also.

*α-Phenylpiperic acid* crystallises from glacial acetic acid in needles, and melts at 208—209°. The *potassium* and *sodium* salts dissolve readily in alcohol; the *magnesium* salt is amorphous.

*Piperonylenemalonic acid*,\*  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:C(COOH)}_2$ , is prepared by treating piperonylacraldehyde with acetic anhydride and sodium malonate, carbonic anhydride being eliminated; if glacial acetic acid is employed in place of the anhydride, no evolution of gas occurs. The substance crystallises from alcohol in small, brick-red needles, and melts at 205—206°. The *calcium* salt crystallises in microscopic needles, and the *silver* salt is amorphous. On heating the acid above its melting point, carbonic anhydride is evolved and piperic acid is formed. When reduced with sodium amalgam, it yields *dihydropiperonylenemalonic acid*,



\* The author gives the name "piperonylene" to the group



which melts and loses carbonic anhydride at  $121^{\circ}$ . The *diethylic* salt of piperonylenemalononic acid is prepared in the usual manner from piperonylacraldehyde and ethylic malonate; it crystallises in golden-yellow leaflets, and melts at  $106\text{--}107^{\circ}$ .

*Piperonylenepyruvic acid*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:CH:CO}\cdot\text{COOH}$ , separates from hot water in small, reddish-yellow needles, which are brick-red when dry; it sinters at  $150^{\circ}$ , and melts at  $165\text{--}167^{\circ}$ . It dissolves sparingly in cold water, more readily, however, in alcohol and hot water; it differs from the foregoing compounds in its behaviour towards concentrated sulphuric acid, this reagent giving rise to a violet coloration.

*Piperonylvinyketocarboxylic acid*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CO}\cdot\text{COOH}$ , is obtained on heating piperonal with a mixture of pyruvic and acetic acids; it separates from hot water in the form of a yellow, micro-crystalline precipitate. It sinters at  $140^{\circ}$ , and melts at  $148\text{--}150^{\circ}$ ; concentrated sulphuric acid develops a blood-red coloration. The *phenylhydrazone* crystallises from alcohol in dark red needles, and melts at  $155^{\circ}$ .

*Piperonyleneacetone*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:CH:CO}\cdot\text{Me}$ , is formed on adding a few drops of aqueous alkali to a solution of piperonylacraldehyde in acetone; it crystallises in needles, and melts at  $89^{\circ}$ . The *phenylhydrazone* crystallises from alcohol in yellowish-brown needles, and melts at  $141^{\circ}$ .

*Dipiperonyleneacetone*,  $(\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:CH})_2\text{CO}$ , is obtained by condensing the foregoing compound with a further molecular proportion of piperonylacraldehyde. It crystallises from hot glacial acetic acid in red, stellate needles, and is orange-red when dry; it melts at  $198\text{--}199^{\circ}$ , and develops a violet coloration with concentrated sulphuric acid. The *phenylhydrazone* crystallises from alcohol in yellow needles, and melts at  $58\text{--}60^{\circ}$ .

*Piperonyleneacetophenone* crystallises in golden-yellow leaflets, and melts at  $133^{\circ}$ ; the *phenylhydrazone* melts at  $49\text{--}50^{\circ}$ .

When piperic chloride and piperidine are brought together in benzene, piperine is formed; syntheses of homologous derivatives of piperine may be effected in a similar manner.

*Methylpiperine*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CH:CMe}\cdot\text{CO}\cdot\text{C}_5\text{NH}_{10}$ , is obtained on adding a solution of piperidine in benzene to a mixture of methylpiperic acid and phosphorus pentachloride which has been heated on the water bath, and subsequently dissolved in benzene. It forms colourless, rhombic crystals, and melts at  $125\text{--}126^{\circ}$ . Methylpiperine is insoluble in light petroleum, but dissolves readily in other organic solvents; it is feebly basic in character, and has a peppery taste.

*Ethylpiperine* forms compact, colourless crystals, and melts at  $118\text{--}119^{\circ}$ ; *phenylpiperine* melts at  $134^{\circ}$ .

*Methylenecaffeic piperide*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CH:CO}\cdot\text{C}_5\text{NH}_{10}$ , is prepared from methylenecaffeic acid (Lorentz, Abstr., 1881, 48) by the method employed for the production of methylpiperine. It is very readily soluble in alcohol, from which it separates in snow-white crystals; it melts at  $80^{\circ}$ .  
M. O. F.

**Hop Tannin and Phlobaphene.** By MICHAEL M. HAYDUCK (*Bied. Centr.*, 1895, **24**, 285; from *Woch. Brauerei*, 1894, **11**, 409).—Tannin was separated from hops by Etti's method (this Journal, 1876, i, 927). It is a light brown powder, soluble in water, alcohol, and ethylic acetate. The solution gives an intense green colour, without precipitation, with ferric chloride. Phlobaphene, a red-brown powder, only very sparingly soluble in water or alcohol, gives a dirty green precipitate; it precipitates albumin. The amount of tannin in hops is best estimated by Lowenthal's method as improved by Schröder.

A solution of tannin precipitated a barley extract (previously boiled), and the precipitate redissolved on heating; phlobaphene, on the other hand, gave a precipitate which did not dissolve on heating.

Both substances act indirectly as preservatives in brewing, in removing most of the more readily decomposable matters.

N. H. J. M.

**Cinnamylidenemalonic acid and the Stereoisomeric Cinnamylideneacetic acids.** By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1433—1443; compare *Abstr.*, 1894, i, 173).—Cinnamylidenemalonic acid is distinctly yellow in colour, but when exposed to sunlight for two or three weeks becomes white, and at the same time much more soluble in alcohol, and is found to melt indefinitely about 30° lower than the yellow acid. No loss of weight occurs during the change, and the exact nature of the white acid has not yet been ascertained. When cinnamylidenemalonic acid is heated with an excess of quinoline at 160—170°, two monobasic acids are formed, the one described by Perkin, which melts at 165°, being accompanied by an isomeric acid melting at 138°. The latter acid forms almost the sole product when the cinnamylidenemalonic acid is heated with exactly 1 mol. of quinoline.

*Allocinnamylideneacetic acid*, prepared in this way, crystallises in needles melting at 138°, and is much more readily soluble in the usual solvents than the previously-known acid. The salts of the allo-acid are also much more easily soluble than those of the isomeric acid. The allo-acid is quantitatively converted into the ordinary acid when its solution in benzene is boiled with a little iodine for a short time; the same change occurs when the solution in benzene containing iodine is exposed to sunlight (compare this vol., i, 454).

A. H.

**Addition of Aromatic Bases to Ethereal Salts of Benzylidenemalonic and Furfurylidenemalonic acids.** By I. GOLDSTEIN (*Ber.*, 1895, **28**, 1450—1455).—*Ethylic  $\beta$ -anilidobenzylmalonate*,  $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}(\text{COOEt})_2$ , is obtained by the direct combination of aniline with ethylic benzylidenemalonate in benzene solution. It forms colourless, silky needles melting at 98—100°. The *hydrochloride* is a white, crystalline powder.

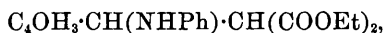
*Ethylic  $\beta$ -phenylhydrazidobenzylmalonate* forms prisms which melt at 79—80°, and yields a crystalline *hydrochloride*. When it is heated above its melting point, it decomposes, with formation of ethylic malonate and benzylidenehydrazone. *Ethylic  $\beta$ -phenylhydrazido-*

benzylmalonate is decomposed by alcoholic potash, yielding the *potassium salt of  $\beta$ -phenylhydrazidobenzylmalonic acid*, which is a yellow, crystalline powder. The free acid does not appear to exist, and when a solution of the potassium salt is acidified, an immediate precipitate of benzylidenehydrazone is obtained. Ethylic  $\beta$ -anilidobenzylmalonate behaves in a similar manner towards alcoholic potash, the *potassium salt of  $\beta$ -anilidobenzylmalonic acid* being obtained in readily soluble, white needles.

Benzylidenemalononic acid itself does not form additive compounds with aromatic bases.

Ethylic  $\beta$ -*paratoluidobenzylmalonate* forms white needles melting at 80–82°. The corresponding *ortho-compound* crystallises in prisms, which melt at 67·5°.

Ethylic  $\beta$ -*anilidofurfurylidenemalonate*,



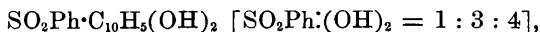
crystallises in prisms, which melt at 72–73°.

A. H.

**Etherification of Mellitic acid and of the two Hydromellitic Acids.** By J. VAN LOON (*Ber.*, 1895, 28, 1270–1274).—Wöhler and Schwarz found that no ethereal salt is formed by the action of hydrogen chloride on mellitic acid in alcoholic solution. The author confirms this result, which is in agreement with Victor Meyer's rule. The two hydromellitic acids, after treatment in methylic alcoholic solution with hydrogen chloride, yielded products which, when dry, had an acid reaction; they were hydrolysed with potash, and the solution tested for methylic alcohol: in the case of hydromellitic acid with negative, in that of isohydromellitic acid with positive, results. Analysis of the silver salt showed that the isohydromellitic acid had been converted into a monomethylic derivative. These facts are also in full accordance with Victor Meyer's rule, and they suggest that in isohydromellitic acid only one carboxyl group is in the "trans" position, and that consequently a trimethylic salt might, with some difficulty, be obtained, but the attempts hitherto made have been unsuccessful.

J. B. T.

**Derivatives of Diphenylsulphone and of Phenyl-naphthylsulphone.** By OSCAR HINSBERG (*Ber.*, 1895, 28, 1315–1318; compare this vol., i, 144).—The following compounds were prepared by bringing the finely powdered quinone into excess of a cold aqueous solution of benzenesulphinic acid. *Dihydroxymethylpropyldiphenylsulphone*,  $[\text{SO}_2\text{Ph} : \text{Me} : \text{Pr} : (\text{OH})_2 = 6 : 1 : 4 : 2 : 5]$ , from thymoquinone, melts at 136°. *Dihydroxyphenyl-naphthylsulphone*,

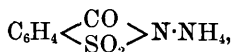


from  $\beta$ -naphthaquinone, melts and decomposes at about 185°; its *dibenzyl derivative* melts at 178°. *Hydroxydimethylamidophenylamidophenyl-naphthylsulphone*,  $\text{SO}_2\text{Ph}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , from naphthol-blue, forms greenish crystals (? colourless when pure); its yellowish *hydrochloride* decomposes at about 220°.

C. F. B.

**Two Isomeric Chlorides of Orthosulphobenzoic acid.** By IRA REMSEN (*Amer. Chem. J.*, 1895, **17**, 309—311).—Orthosulphobenzoic chloride is found to consist of two isomeric compounds, the *symmetrical*,  $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , and the *unsymmetrical*,  $\text{C}_6\text{H}_4\langle\text{CCl}_2\rangle\text{SO}_2$ .

The one, which is probably the symmetrical compound, forms crystals melting at  $76^\circ$ , and is probably identical with the chloride described by Remsen and Dohme (*Abstr.*, 1889, 992); the other, the unsymmetrical, melts at  $21.5\text{--}22.5^\circ$ . Both yield the same orthosulphobenzoic acid when treated with water. With ammonia, the chloride of higher melting point yields benzoic sulphinide,



whilst the unsymmetrical chloride yields ammonium orthocyanobenzenesulphonate,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{NH}_4$ . Ammonia, water, and alkalis all act more readily on the unsymmetrical than on the symmetrical compound. With benzene and aluminium chloride, orthobenzoylbenzenesulphonic chloride,  $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , is first formed, and, on continued action, orthobenzoyldiphenylsulphone,  $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ph}$ . This latter, when fused with potash, yields diphenylsulphone and benzoic acid. The phenols act on both chlorides, yielding coloured substances, and also the phenyl salts of orthosulphobenzoic acid. The latter reactions are being further investigated. See also three following abstracts.

L. T. T.

**Action of Aniline and of the Toluidines on Orthosulphobenzoic acid and its Chlorides.** By IRA REMSEN and CHARLES E. COATES, jun. (*Amer. Chem. J.*, 1895, **17**, 311—330).—Several of the salts of this acid are described. *Aniline orthosulphobenzoate*,



forms transparent, colourless needles or prisms, which melt at  $165^\circ$ , and begin to decompose at  $185^\circ$ . It is moderately soluble in boiling water, but this and other analogous salts are partially decomposed on continued boiling of the solution, some of the base being volatilised, and the *acid aniline salt* produced. The latter salt crystallises with 1 mol. aq. in needles melting at  $108^\circ$ . The *normal paratoluidine salt* forms thick, colourless needles, soluble in boiling water, and melting at  $197^\circ$ . The *acid salt* (with  $\text{H}_2\text{O}$ ) forms very soluble, colourless needles. The *normal metatoluidine salt* crystallises in small, granular crystals melting at  $163.5^\circ$ ; the *acid salt* (with  $\frac{1}{2}\text{H}_2\text{O}$ ) in large, and very soluble, rhombic crystals melting at  $110^\circ$ . The *normal orthotoluidine salt* forms white, easily soluble needles melting at  $127.5^\circ$ ; and the *acid salt* (with  $\frac{1}{2}\text{H}_2\text{O}$ ) in white needles, easily soluble in water and alcohol.

On distillation these salts are for the most part carbonised, but the paratoluidine salt, when distilled at 15 mm. pressure, yields some of the paratolil. The normal salts, when heated for some time at about  $230^\circ$ , give off the base in part, and form gums which may contain the unsymmetrical anil or tolil. The anils and tolils are formed by the

action of the acid chlorides on the bases. They take up water when boiled with dilute alkalis, and form the anilic and tolilic acids, which form definite salts, but lose water, and revert to the anil or tolil respectively when heated above  $200^{\circ}$ . The formation of two anilides of different physical properties, and also of two metatoluidides and probably of two paratoluidides confirms the view (see preceding abstract) that the chloride of orthosulphobenzoic acid is a mixture of two isomeric chlorides, one symmetrical and the other unsymmetrical.

With excess of aniline, orthosulphobenzoic chloride yields a mixture of two isomeric anilides. The *fusible anilide* is best obtained when the action takes place in the presence of water, and at as low a temperature as possible. It crystallises from alcohol in needles, which gradually change, when left in contact with alcohol, into large, flat prisms. Both forms of crystals melt at  $196^{\circ}$ , and are soluble in boiling alcohol. The *infusible anilide* is best formed when the reagents act on one another in the anhydrous state. It crystallises from boiling alcohol with 1 mol. alcohol in orthorhombic crystals, which lose their alcohol slowly at  $130^{\circ}$ , rapidly at  $160^{\circ}$ , turn brown at  $250^{\circ}$ , and melt and decompose to a red liquid at  $270$ – $280^{\circ}$ . Both anilides dissolve in alkalis and alkali carbonates, and are reprecipitated by acids. Neither decompose powdered calcite when boiled therewith.

*Orthosulphobenzanil*,  $C_6H_4<\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}>NPh$ , is usually obtained in small quantity during the formation of the infusible anilide, especially if the crude product is maintained at a moderately high temperature for some time. It crystallises in long, white, flat blades or needles, melting at  $190.5^{\circ}$ . These crystals are soluble in hot alcohol and hot ether, sparingly so in hot chloroform, and are insoluble in water and alkalis. When boiled for some time with aqueous alkalis, they yield the *anilic acid*, which forms granular crystals soluble in alcohol, alkalis, and alkali carbonates, and in much boiling water. The *barium salt* (with  $H_2O$ ) crystallises in needles. *Orthosulphobenzoparatolil* crystallises in thin needles melting at  $195.5^{\circ}$ , and yields the *tolilic acid* melting at  $155^{\circ}$ . *Infusible orthosulphobenzoparatoluidide* crystallises in anhydrous, transparent cubes, which are unchanged at  $250^{\circ}$ , and decompose at higher temperatures. The *fusible paratoluidide* was only obtained in very small quantity, but apparently forms needles melting at  $196^{\circ}$ . *Orthosulphobenzometatolil* crystallises in needles or prisms melting at  $147.5^{\circ}$ . The *fusible metatoluidide* crystallises in large grains, melting at  $161.5$ – $162.5^{\circ}$ ; the *infusible metatoluidide*, with 1 mol. alcohol, in prisms which lose alcohol at  $120^{\circ}$ , but remain solid at  $250^{\circ}$ . *Orthosulphobenzo-orthotolil* yields short, thick needles or plates, melting at  $172$ – $175^{\circ}$ . Only one orthotoluidide was obtained, and that with difficulty, and in small quantity. It appears to be the *infusible orthotoluidide*, and to crystallise with 2 mols. alcohol. (See also preceding abstract.)

L. T. T.

**Action of Aniline on the Chlorides of Orthosulphobenzoic acid.** By IRA REMSEN and E. P. KOHLER (*Amer. Chem. J.*, 1895, 17, 330–347).—This is a continuation of the work of Remsen and Coates (see preceding abstract). Attempts to separate the two

isomeric chlorides by crystallisation proved futile; but when the mixed chlorides are treated with cold water for some hours crystals form, and may be separated. These crystals are then stable, may be recrystallised from ether or chloroform, and melt at  $76^{\circ}$ . This substance is probably the symmetrical chloride,  $\text{SO}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , and is identical with that described by Remsen and Dohme (Abstr., 1889, 992). When heated at  $150^{\circ}$ , or in the presence of phosphorus pentachloride at  $100^{\circ}$ , this substance is decomposed, yielding chlorobenzoic chloride. When aniline acts on the mixed chlorides, about three times as much of the infusible anilide is formed as of the fusible. Aniline acting on the solid chloride (m. p.  $76^{\circ}$ ) in the presence of water yields the fusible anilide in almost theoretical proportion, whilst in the absence of water at  $100^{\circ}$ , only the anil and aniline hydrochloride are formed. When a solution of the anil in aniline is boiled for some hours, the fusible anilide is formed. The fusible anilide dissolves unchanged in alkalis, but if the alkaline solution is boiled for some time, orthosulphobenzoic acid is formed. It is probably the symmetrical compound  $\text{NHPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$ . The infusible anilide is more resistant towards reagents than the fusible anilide is, and even after continued boiling is reprecipitated from its alkaline solutions unchanged on the addition of an acid. When boiled with benzoic chloride, it yields benzanilide. *Aniline orthosulphanilidobenzoate*,  $\text{NHPh}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{NH}_2\text{Ph}$ , crystallising in colourless prisms, is also formed in small quantities during the action of aniline on the chlorides.

L. T. T.

**Separation of the two Chlorides of Orthosulphobenzoic acid.** By IRA REMSEN and A. P. SAUNDERS (*Amer. Chem. J.*, 1895, 17, 347—368; see also three preceding abstracts).—The authors have succeeded in separating these chlorides as follows. The mixed chlorides are treated with light petroleum, and the solution at about  $30^{\circ}$  is poured off from excess of the chlorides. On cooling this solution to a low temperature, the two chlorides crystallise out, the higher melting chloride (m. p.  $76$ — $77^{\circ}$ ) in square hollow crystals, the lower melting chloride (m. p.  $21.5$ — $22.5^{\circ}$ ) in radiating clusters of delicate, glistening, white needles. The chloride of low melting point even then generally contains some of the isomeride. The crystallisation is best effected by spontaneous evaporation of the petroleum solution in the open air at  $0^{\circ}$ , or in a current of air at the same temperature. When a chloroform solution of the mixed chlorides is shaken with concentrated aqueous ammonia, the chloride of m. p.  $21.5^{\circ}$  is completely converted into a substance soluble in water, but the chloride of m. p.  $76^{\circ}$  is but little attacked. In this way the high melting chloride can be readily obtained pure.

Water acts very slowly on both chlorides, but the same acid is produced in each case. With aqueous ammonia, the liquid chloride yields a sweet substance of the probable formula  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ . This substance crystallises in minute needles melting at  $116$ — $120^{\circ}$ , and having a bitter taste. With dry ammonia, this substance is also produced together with "saccharin." No similar compounds could be obtained from the high melting chloride. With phenol, both chlo-



rides yield *diphenylic orthosulphobenzoate*, which crystallises in needles melting at 117·5—118·5°, but has a tendency to pass into a coloured substance like phenolphthaleïn. It is, however, doubtful whether its formation from the low boiling chloride is not due to the presence therein of the high melting chloride. By the action of benzene and aluminium chlorides, both chlorides yield first the compound  $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , and finally, with excess,  $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ph}$ . The former compound yields with potash, *potassium orthobenzoylbenzenesulphonate*, melting at 122—124° when heated quickly, at about 175° when heated slowly. The *ethylic salt* is crystalline, but very unstable. The *acid* crystallises in needles melting at 143—145°. Ammonia forms a *lactime*.

The results leave little doubt that the chloride of m. p. 76—77° has the symmetrical formula, and therefore the chloride of m. p. 21·5—22·5° is probably the unsymmetrical compound. L. T. T.

**Action of Nitrous acid on Indene and Coumarone.** By MAXIMILIAN DENNSTEDT and CÆSAR AHRENS (*Ber.*, 1895, **28**, 1331—1335).—When nitrous acid is led into a cooled ethereal solution of indene, the latter reacts like cinnamene (this vol., i, 456), and yields an  $\alpha$ -nitrosite, which melts at 107—109°, and is converted by boiling with absolute alcohol into the  $\beta$ -nitrosite, melting at 136—137°; yellow needles are also obtained of a compound,  $\text{C}_9\text{H}_7\text{NO}_2$ , very much resembling phenylnitroethylene in appearance; it melts at 141°. Coumarone behaves in a similar fashion, and yields yellow crystals, melting at 126°, of a compound that also resembles phenylnitroethylene; yellow needles, melting at 146—147°, are also obtained, together with the  $\alpha$ -nitrosite, which melts at 114—116°. On account of this similarity of behaviour, indene and coumarone must have a similar constitution; it is not impossible that they may be  $\text{C}_6\text{H}_4\text{<} \begin{smallmatrix} \text{C}:\text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$  and  $\text{C}_6\text{H}_4\text{<} \begin{smallmatrix} \text{C}:\text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$  respectively.

C. F. B.

**A New Synthesis of 2':3'-Dimethylindole.** By KARL BRUNNER (*Monatsh.*, 1895, **16**, 183—189).—The substance previously obtained (*Monatsh.*, 1894, **15**, 747) by the action of zinc chloride on the phenylhydrazone of isobutyrylformic acid, and described as scatole, is now shown to be 2':3'-dimethylindole. The same indole derivative has been prepared from *isobutylidenephénylhydrazine*. This is a yellow oily substance which does not solidify at 0°. It distils at 178—180° under a pressure of 68 mm., and rapidly oxidises when exposed to the air. Small quantities of 2':3'-dimethylindole are obtained when the hydrazone is treated with a mixture of sulphuric acid and alcohol. The yield, however, is much better when the hydrazone is heated with twice its weight of powdered zinc chloride at 140—150°. After recrystallisation from light petroleum, the dimethylindole melted at 99°, and was further identified by means of its nitroso-compound and picrate.

J. J. S.

**Benzophenoneoxime.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1894, **13**, 429—432).—Benzophenoneoxime oxidises spon-

taneously in air to a brown, oily liquid, from which nitric acid and a labile modification of benzophenone can be separated, the latter either by distillation under low pressure with steam or by merely washing with dilute alkali. The action does not take place in an atmosphere of carbonic anhydride, and only very slowly in presence of pure oxygen; in the presence of a small quantity of nitric acid, however, the oxygen is absorbed much more rapidly. The same oxidation is brought about by alkaline permanganate, but with alkaline ferricyanide a colourless oil is obtained, which, except in the presence of nitrous acid, is oxidised by a further quantity of the reagent to a blue liquid soluble in ether.

*Labile benzophenone* is a colourless oil, boiling at 216—220° (25 mm.), and is converted into the ordinary modification, with development of heat, by the addition of a crystal of the latter. JN. W.

### Formation of Acridine from Orthonitrodiphenylmethane.

By OTTO FISCHER (*Ber.*, 1895, **28**, 1335—1337; compare this vol., i, 52).—The view previously entertained, that the formation of acridine and hydracridine by the action of orthonitrobenzylic chloride on benzene in the presence of aluminium chloride is due to the oxidation of amidophenylmethane formed by the reducing action of the aluminium chloride, is confirmed by the fact that acridine and hydracridine are also formed by the reduction of nitrodiphenylmethane by the usual methods. In these cases, the oxidation is effected by a portion of the unaltered nitro-compound. A. H.

**Hexamethyltriamidotriphenylmethane.** By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1895, **120**, 740—743).—The iodoamido-derivatives of hexamethyltriamidotriphenylmethane previously described (this vol., i, 377), can be accurately estimated by means of standard acid solutions. Sodium hydroxide produces partial substitution of hydroxyl for iodine, but the change is limited by an inverse reaction, and the liquid contains a mixture of methiodide and the amidobase. Silver oxide, on the other hand, acts completely, with formation of the compound  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3 + 3\text{H}_2\text{O}$ , which can be accurately titrated with an acid. The alkalinity of these bases is comparable with that of tetrethylammonium hydroxide. The three bases (1)  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{OH}$ , (2)  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{OH})_3$ , and (3)  $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{OH})_3$  have practically the same properties, so far as their basicity is concerned, and they all decolorise magentas.

There are, however, considerable differences between the basic functions as measured by their behaviour with acids, and whether the phenylic carbinol has been converted into an amido- or an ammonium-derivative, the alcoholic function is modified. In the amido-compound,  $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3$ , the alcoholic function is the first to react; in the ammonium compounds the ammoniacal function acts first, whilst the alcoholic function no longer reacts with acids, but only with alcohols, to form ethereal salts; and in the amido-ammonium compounds the ammoniacal function acts first, and the alcoholic and amido-functions act almost simultaneously, but when equilibrium

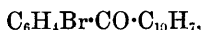
is established the alcoholic function is found to preponderate over that of the amine. C. H. B.

**The Fluorindines.** By RUDOLF NIETZKI (*Ber.*, 1895, **28**, 1357—1360).—Tetramidobenzene condenses with benzile to form a diorthodiazine of the formula  $\begin{array}{c} \text{CPh:N} \\ | \\ \text{CPh:N} \end{array} > \text{C}_6\text{H}_2 < \begin{array}{c} \text{N:CPh} \\ | \\ \text{N:CPh} \end{array}$  (Abstr., 1889, 604).

This substance, on reduction with zinc dust and acetic acid, yields a blue colouring matter, the *hydrochloride* of which can be obtained in the crystalline form. This is not fluorescent, and is converted by oxidation into the original azine from which it was prepared. It is, therefore, not a fluorindine, although it is the first reduction product of the azine, and must have the formula which Fischer and Hepp (*Abstr.*, this vol., i, 220) ascribe to the fluorindines.

The author further replies to the critical remarks of Fischer and Hepp on several points connected with the constitution and properties of the fluorindines. A. H.

**Orthobromophenylnaphthyl Ketone.** By R. J. KNOLL and PAUL COHN (*Monatsh.*, 1895, **16**, 207—210).—The ketone,



was obtained by the action of fresh aluminium chloride on a solution of orthobromobenzoic chloride and naphthalene in carbon bisulphide. It was purified by digesting with warm alcohol, and allowing the solution to remain. It forms colourless, monoclinic prisms, sparingly soluble in alcohol and light petroleum, and melts at 89°.

The *sulphonic acid*, which was obtained on warming the ketone with concentrated sulphuric acid, forms colourless needles, which melt at 143°, and dissolve readily in hot water. The *oxime* melts at 154—156°. J. J. S.

**Naphthazarin.** By CARL T. LIEBERMANN (*Ber.*, 1895, **28**, 1455—1458).—The author maintains that his previously published experiments fully proved the constitution of naphthazarin, which has only been confirmed by the researches of Zincke and Schmidt (*Annalen*, **286**, 27). The most elegant proof of the constitution of this substance is its preparation from 1 : 2 : 1' : 4-tetranitronaphthalene by Will. *Tetrahydroxydihydronaphthalene*,  $\text{C}_{10}\text{H}_6(\text{OH})_4$ , is obtained by reducing naphthazarin with tin and acetic and hydrochloric acids. It crystallises in needles melting at 200°. A. H.

**Pinene.** By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 1344—1353).—The authors have studied the oxidation products of pinene, the crude oil obtained from French oil of turpentine having been used, and only the chief products of the various reactions examined. When oxidised with neutral potassium

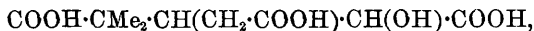
permanganate solution, pinene,  $\text{C} \begin{array}{l} \nearrow \text{CHMe} \cdot \text{CMe}_2 \\ \text{---} \text{CH}_2 \text{---} \\ \searrow \text{CH} \text{---} \text{CH}_2 \end{array} \text{CH}$ , is converted

into *pinonic acid*,  $\text{CHMe} \begin{array}{c} \text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{COOH} \\ \text{CO} - \text{CH}_2 \end{array}$ , which is a colourless oil, boiling and slightly decomposing at  $310-315^\circ$ . The acid is of a ketonic nature, and yields a mixture of two isomeric *oximes*,  $\text{C}_{10}\text{H}_{16}\text{O}_2 \cdot \text{N} \cdot \text{OH}$ , when treated with hydroxylamine. One of these melts at  $125^\circ$  with loss of water, the other at  $160^\circ$  without loss of water. Pinonic acid is not decomposed by alkaline hypobromite with formation of bromoform and a dicarboxylic acid. When it is treated with nitric acid of sp. gr. 1.18, it yields terebic acid, melting at  $174^\circ$ , and oxalic acid. When oxidised with chromic acid, on the other hand, pinonic acid yields, in addition to terebic acid, isocamphoronic acid,  $\text{COOH} \cdot \text{CMe}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{COOH})_2$ , and the dibasic ketonic acid, melting at  $128-129^\circ$ , which has been described by Thiel (Abstr., 1893, i, 423) as isohydroxycamphylic acid, but which the authors name *isoketocamphoric acid*,  $\text{COMe} \cdot \text{CMe}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{COOH})_2$ . This acid yields an oxime, and is decomposed by alkaline hypobromite into carbon tetrabromide and isocamphoronic acid.

When pinonic acid is further treated with alkaline potassium permanganate solution on the water bath, it yields a number of interesting oxidation products, some of which are identical with substances which have been observed among the oxidation products of camphor. From the solution of the product in chloroform, crystals are deposited which consist of *dimethyltricarballic acid*,



which melts at  $147^\circ$ , and when heated above its melting point loses water and yields *anhydrodimethyltricarballic acid*, which forms white crystals melting at  $142.5^\circ$ . The filtrate from the dimethyltricarballic acid contains hydroxytrimethylsuccinic acid, which melts at  $141^\circ$ , and is converted into trimethylsuccinic acid, melting at  $145^\circ$ , by hydriodic acid. The hydroxytrimethylsuccinic acid is accompanied by a lactonic acid, which melts at  $143.5^\circ$ , and is termed by the authors *isocamphoronic acid*,  $\text{C}_9\text{H}_{12}\text{O}_6$ . When it is warmed with alkalis, it yields the salts of the tribasic *hydroxyisocamphoronic acid*,



which has been prepared in the impure state by Kachler (*Annalen*, 191, 152) from camphor. Isocamphoronic acid seems to be isomeric with the isocamphorenic acid melting at  $226^\circ$ , obtained by Kachler from isocamphoronic acid by heating with bromine. All these reactions are well expressed by the formulæ given above, which are consistent with the formula recently proposed for camphor by Tiemann (this vol., i, 428).

A. H.

**Limonene Nitrosochlorides.** By OTTO WALLACH (*Ber.*, 1895, 28, 1308—1315).—The molecular weight of  $\alpha$ - and  $\beta$ -limonene nitrosochlorides have been redetermined in consequence of Baeyer's results (this vol., i, 380). In phenol solution, at the melting point, both are mono-molecular; in benzene solution, at the melting point, the  $\beta$ -compound is bi-molecular, the  $\alpha$ -compound partly bi- and partly mono-molecular; the latter is not entirely mono-molecular, even at

the boiling point of the solution. Limonene nitrolanilides, both  $\alpha$ - and  $\beta$ -, are mono-molecular in benzene solution, both at the freezing point and at the boiling point. C. F. B.

### Action of Hydrogen Peroxide on Coniine and $\beta$ -Pipicoline.

By RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 1459—1466).—The preparation of an amido-aldehyde from coniine by the method used for piperidine (*Abstr.*, 1894, i, 143) does not succeed because of the insolubility of the base. When coniine and hydrogen peroxide are brought together, however, in acetone solution,  $\alpha$ -propyl- $\delta$ -amidovaleraldehyde,  $\text{NH}_2\cdot\text{CHPr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$ , is produced. It is a colourless syrup, which boils at about 103—105° (at 10 mm. pressure), and has a characteristic odour, quite distinct from that of coniine. It has sp. gr. = 0.9414 at 20°, and the specific rotation  $[\alpha]_D = +59.95^\circ$ . The substance shows the usual reducing properties of an aldehyde, and forms a deliquescent hydrochloride,  $\text{C}_8\text{H}_{17}\text{NO}\cdot\text{HCl}$ . Coniine preparations which have been preserved for some time often show slight reducing properties, which are probably due to the formation of a small amount of the aldehyde by the action of the oxygen of the air. When the amido-aldehyde is distilled with potash, it loses water and forms a mixture of coniine and coniceïne. Coniceïne is sometimes formed directly by the action of hydrogen peroxide on an acetone solution of coniine, the base thus produced being different from  $\gamma$ -coniceïne. When the hydrochloride of the aldehyde is treated with sodium hydrogen sulphite, conienesulphonic acid is precipitated as an oil which soon solidifies to white needles melting at 135°.

In the preparation of the aldehyde from coniine, a certain amount of butyrylbutyric acid,  $\text{C}_3\text{H}_7\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , and some acetic acid, is also produced. The former of these melts at 34°, boils at 280—285°, and yields a syrupy oxime.  $\beta$ -Pipicoline may be converted in a similar way into  $\beta$ -methyl- $\delta$ -amidovaleraldehyde, which forms a hydrochloride melting at 139°, and a picrate which melts at 84°.

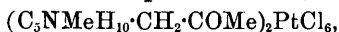
A. H.

**Piperidylacetal.** By RICH. STOERMER and O. BURKERT (*Ber.*, 1895, **28**, 1247—1249; compare *Abstr.*, 1894, i, 556).—The base is most readily purified by means of the ferrocyanide, it is easily soluble, and resembles coniine, being precipitated as an oil when its aqueous solution is warmed. The hydrobromide and the additive compounds with propylic bromide and allylic iodide are colourless, crystalline, and extremely deliquescent. The methiodide and ethiodide melt at 121° and 105° respectively, not at 119° and 123°, as previously stated. The picrate crystallises in small, yellow needles, and melts at 67°. All attempts to prepare piperidyl aldehyde were unsuccessful. By the action of moist silver oxide on the above methiodide, and distillation of the aqueous solution, a colourless liquid base is obtained; it boils at 220°, has an extremely unpleasant fishy smell, and yields only oily salts; it probably corresponds in constitution with dimethylpiperidine, and has the formula  $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_3\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ .

J. B. T.

**Piperidylacetone.** By RICH. STOERMER and O. BURKERT (*Ber.*, 1895, **28**, 1250—1252).—Chloracetone and piperidine readily react at

the ordinary temperature, forming *piperidylacetone*,  $C_5NH_{10} \cdot CH_2 \cdot COMe$ , a colourless liquid with a somewhat pleasing smell. It boils at  $195-197^\circ$  (uncorr.), gradually becomes yellow, and reduces Fehling's solution and silver solution at ordinary temperatures; the base dissolves in water and the solution becomes turbid when warmed. The yield is 85 per cent. of the theoretical. The *hydrochloride*,  $C_5H_{15}NO \cdot HCl$ , and the *hydrobromide* are very deliquescent. The *platinochloride* crystallises in large, broad, orange-coloured prisms, and melts at  $192-193^\circ$ . The *aurochloride* is deposited in slender, pale yellow plates, melting at  $107-108^\circ$ . The *methiodide* is crystalline, and melts at  $126^\circ$ . The *oxime* crystallises from water in long needles, from light petroleum in small plates, and melts at  $104-105^\circ$ . The *phenylhydrazone* crystallises in pale yellow plates melting at  $59-62^\circ$ , it is stable in air, but decomposes in a desiccator. The preparation of methylacetylpiperidine by the action of moist silver oxide on the methiodide could not be accomplished, part of the quaternary base is oxidised by the silver oxide, and the remainder is decomposed during the distillation. The *ammonium hydroxide* yields a *chloride* from which the *platinochloride*,



and the *aurochloride* are obtained; both crystallise readily, and melt at  $218-219^\circ$  and  $85^\circ$  respectively. J. B. T.

**Synthesis of  $\beta$ -Propylpiperidine.** By J. DARNELL GRANGER (*Ber.*, 1895, **28**, 1197—1204; compare R. Funk, *Abstr.*, 1894, i, 34).—*Ethyl  $\gamma$ -phenoxydipropylmalonate*,  $OPh \cdot C_3H_5 \cdot CPr^2(COOEt)_2$ , is obtained by heating ethyl  $\gamma$ -phenoxypropylmalonate (*loc. cit.*) with propylic iodide and sodium dissolved in propylic alcohol; it is a colourless, viscous liquid, which boils at  $282-283^\circ$  under a pressure of 100 mm. On hydrolysis with alcoholic potash, it yields the *acid* which sinters at  $95^\circ$ , and melts and decomposes at  $104-106.5^\circ$ . The *ammonium* and *silver* salts are amorphous, the *calcium* salt is crystalline.

When  $\gamma$ -phenoxydipropylmalonic acid is heated at  $180-200^\circ$ , carbonic anhydride is evolved, and  $\alpha$ -propyl- $\delta$ -phenoxyvaleric acid is formed; it is insoluble in water, and separates from ordinary solvents in large, transparent crystals melting at  $53-54^\circ$ . The *nitrile* is obtained by distilling the acid with lead thiocyanate; it is a yellow oil which boils at  $318-322^\circ$ .  $\beta$ -Propyl- $\epsilon$ -phenoxyamylamine is formed on reducing this nitrile; the *picrate* melts at  $112^\circ$ , and the *platinochloride* crystallises in yellow needles. When the base is heated with fuming hydrochloric acid for 15 hours at  $100^\circ$ , the *hydrochloride* of  $\beta$ -propyl- $\epsilon$ -chloramylamine is formed; the *picrate* melts at  $151^\circ$ .

$\beta$ -Propylpiperidine is obtained from the foregoing base by heating the hydrochloride with aqueous sodium hydroxide; it is a colourless oil, with the odour of conine. The vapour produces white fumes when brought into contact with hydrogen chloride; the *picrate* melts at  $121.5^\circ$ , and the *platinochloride* melts at  $94^\circ$  when slowly heated, and at  $134^\circ$  when the temperature rises rapidly. M. O. F.

**$\nu$ -Methyltetrahydroquinoline (Kairolin) and Tetrahydroquinoline Methohydroxide.** By ALBERT LADENBURG (*Ber.*, 1895,

**28**, 1171—1173).—The author establishes the identity of kairoline with the base obtained by Ostermayer on treating tetrahydroquinoline methochloride with alkalis. M. O. F.

**2'-Phenylquinoline.** By AMÉ PICTET and H. BARBIER (*Bull. Soc. Chim.*, 1895, [3], **13**, 26—28).—When acetophenone and formanilide are boiled together for 30 hours, the product is not 4'-phenylquinoline, as might be expected, but the 2'-compound. This is conveniently isolated by means of the *mercurochloride*, a crystalline substance melting at 231°. The free base melts at 85°, and shows all the properties of 2'-phenylquinoline. The mechanism of formation thus resembles that of acridine from formyldiphenylamine, and would seem to point to the existence of a para-bond between nitrogen and carbon in the pyridine nucleus. JN. W.

**Benzylquinoline.** By LEOPOLD RUGHEIMER and W. KRONTHAL (*Ber.*, 1895, **28**, 1321).—*Benzylquinoline*,  $C_9NH_6 \cdot CH_2Ph$ , was prepared by heating benzoyltetrahydroquinoline with benzaldehyde. It crystallises in large tablets, and yields a *hydrochloride*, yellow *platinochloride*, silky *sulphate*, and yellow *picrate*; the last melts at 161.5°. C. F. B.

**Ethylglyoxalidine and Propylglyoxalidine.** By E. KLINGENSTEIN (*Ber.*, 1895, **25**, 1173—1176; compare this vol., i, 73).—*Ethylglyoxalidine*,  $\begin{array}{c} CH_2-N \\ | \\ CH_2-NH \end{array} > CEt$ , is obtained by distilling a mixture of ethylenediamine hydrochloride (10 grams) and sodium propionate (18 grams); it boils at 144—148° under a pressure of 95 mm., and solidifies when cooled. The *hydrochloride* and *hydrobromide* are crystalline and hygroscopic; the *aurochloride* melts at 171—172°, and the *platinochloride* crystallises in reddish-yellow prisms, and melts at 198°. The *mercurochloride* has the composition  $C_5H_{10}N_2 \cdot HCl \cdot 5HgCl_2$ , and melts at 169—171°. The *picrate* melts at 134—136°, and the *benzoyl* derivative at 242°; the *urate* has not been obtained free from uric acid. *Dipropionylethylenediamine* forms the intermediate product in the preparation of ethylglyoxalidine; it melts at 160—162° and boils at 220—230° under a pressure of 95 mm.

*Propylglyoxalidine* is obtained from ethylenediamine hydrochloride and sodium butyrate; it is a colourless, hygroscopic liquid which boils at 134—140° under a pressure of 23 mm., and solidifies when cooled. The *hydrochloride* and *hydrobromide* are hygroscopic; the *aurochloride* melts at 126—127°, and the *platinochloride* crystallises in red prisms melting at 162—164°. The *mercurochloride* melts at 163—165°, and the *picrate* crystallises in long needles, and melts at 124—126°; the *urate* has not been obtained free from uric acid. In preparing propylglyoxalidine by the method indicated, *dibutyryl-ethylenediamine* is also formed. M. O. F.

**Dimethylglyoxalidine and Methylethylglyoxalidine. Resolution of Propylenediamine into its Optical Components.** By GEORG BAUMANN (*Ber.*, 1895, **28**, 1176—1180).—1 : 4-*Dimethylglyox-*

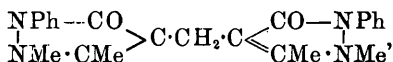
*alidine*,  $\begin{array}{c} \text{CHMe}\cdot\text{NH} \\ | \\ \text{CH}_2\text{---N} \end{array} \gg \text{CMe}$ , is obtained by distilling a mixture of propylenediamine hydrochloride and sodium acetate (2 mols.), the diacetyl-derivative being produced at the same time. The base is a pale yellow liquid which boils at  $125^\circ$  under a pressure of 22 mm.; it is hygroscopic, and is readily miscible with all ordinary solvents. The *benzoyl* derivative melts at  $197^\circ$ , and the *aurochloride* crystallises in yellow leaflets melting at  $175^\circ$ ; the *picrate* melts at  $140^\circ$ , and the *mercurochloride*, which has the composition  $\text{C}_5\text{H}_{10}\text{N}_2\cdot\text{HCl}\cdot 6\text{HgCl}_2$ , melts at  $176^\circ$ .

4:1-*Methylethylglyoxalidine* is obtained from propylenediamine hydrochloride and sodium propionate; it boils at  $130^\circ$  under a pressure of 62 mm., and is readily soluble in water. The *dipropionyl*-derivative is formed at the same time; it crystallises in small, white needles and melts at  $165^\circ$ . The *hydrochloride*, *hydrobromide*, and *tartrate* are hygroscopic syrups, and the *benzoyl*-derivative melts at  $205^\circ$ . The *aurochloride* and *platinochloride* melt at  $125^\circ$  and  $188^\circ$  respectively; the *picrate* melts at  $132^\circ$ , and the *mercurochloride*, which has the composition  $\text{C}_6\text{H}_{12}\text{N}_2\cdot\text{HCl}\cdot 5\text{HgCl}_2$ , melts at  $172^\circ$ .

4-*Methylglyoxalidine* is obtained from propylenediamine hydrochloride and sodium formate; the *aurochloride* melts at  $166\text{--}168^\circ$ , and the other salts are extremely soluble in water.

Lævorotatory propylenediamine is obtained from the tartrate which melts at  $141^\circ$ ; the specific rotatory power is  $-19\cdot 11^\circ$  at  $24\cdot 3^\circ$ . The *picrate* forms yellow crystals and melts at  $237^\circ$ . M. O. F.

**Antipyrine Derivatives.** By ADOLF SCHUFTAN (*Ber.*, 1895, 28, 1180—1187).—*Methylenediantipyrine*,



is obtained by heating a mixture of antipyrine and formaldehyde at  $120^\circ$ ; it is also formed when benzyldenediantipyrine (*loc. cit.*) is heated in sealed tubes with formaldehyde and zinc chloride for six hours at  $120^\circ$ . It crystallises in white, lustrous leaflets, and melts at  $177^\circ$ . The *hydrochloride* and *sulphate* crystallise in colourless needles; the *platinochloride* forms long, reddish-yellow needles, and becomes black at  $200^\circ$ , without undergoing fusion. The *aurochloride* crystallises in reddish-brown plates, melting and decomposing at  $179^\circ$ ; the *picrate* melts at  $185^\circ$ , and the *tetrabromide* forms pale yellow needles, which melt and decompose at  $140^\circ$ .

*Ethylidenediantipyrine* crystallises in white nodules, and in the anhydrous state melts at  $153^\circ$ ; a specimen dried in the exsiccator melted at  $110^\circ$ , losing  $1\text{H}_2\text{O}$ . The *hydrochloride* crystallises in slender, white needles, and melts at  $134^\circ$ , the sulphate is sparingly soluble in cold water, and separates from dilute sulphuric acid in slender needles. The *platinochloride* does not melt at  $200^\circ$ , at which temperature, however, it turns black; the *picrate* crystallises in yellow needles.

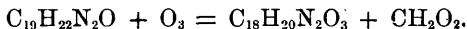
*Hydroxybenzyldenediantipyrine* is obtained on heating a mixture



of antipyrine and salicylaldehyde for eight hours at  $120^{\circ}$ . The base separates from methylic alcohol in colourless, transparent prisms, and contains  $1\text{H}_2\text{O}$ , which is not lost at  $110^{\circ}$ ; it melts at  $180\text{--}190^{\circ}$ . The *hydrochloride* crystallises in colourless needles, and the *picate* in yellow needles which melt and decompose at  $216^{\circ}$ ; the *platinochloride* forms reddish-yellow needles.

M. O. F.

**Cinchonine and Cinchotenine.** By ZDENKO H. SKRAUP (*Monatsh.*, 1895, **16**, 159—179; compare *Abstr.*, 1880, 409).—Cinchotenine is obtained by oxidising cinchonine with potassium permanganate.



Formic acid is the other product of oxidation, and this shows that one of the carbon atoms of cinchonine must be in a more exposed position than the others. According to Schützenberger, cinchonine contains a hydroxyl group, as it yields a benzoyl derivative. The author shows that this hydroxyl is also contained in cinchotenine, since benzoylcinchonine when oxidised gives benzoylcinchotenine. Cinchotenine further contains a carboxyl group, and reacts as a saturated compound; cinchonine, on the other hand, reacts as an unsaturated compound, and contains no carboxyl group. The two are best represented as follows.



Cinchonine.



Cinchotenine.

*Benzoylcinchonine* melts at  $75^{\circ}$ , and is very soluble in ether and benzene. It is slowly hydrolysed by boiling acids, much more readily by alkalis. The *hydrochloride*,  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{OBz}\cdot\text{HCl}$ , crystallises in long needles, which melt at  $206\text{--}207^{\circ}$ . The dihydrochloride,  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{OBz}\cdot 2\text{HCl}$ , loses hydrogen chloride at  $120^{\circ}$ . The disulphate is amorphous, and is not decomposed by heating to  $140^{\circ}$ , whereas cinchonine disulphate itself is readily decomposed at this temperature, and yields cinchonine.

*Benzoylcinchotenine*,  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{OBz}$ , does not readily crystallise if it contains traces of impurities. When quite pure, it forms short, colourless prisms, which melt at  $175\text{--}178^{\circ}$ . It forms a crystalline hydrochloride, and when hydrolysed gives benzoic acid and cinchotenine.

The *ethylic* salt of *cinchotenine* is readily obtained as a hydrochloride by saturating an alcoholic solution of cinchotenine with dry hydrogen chloride. This *hydrochloride* melts at  $235^{\circ}$ , and the ethylic salt itself at  $210^{\circ}$ . This ethereal salt reacts vigorously with benzoic chloride to form a *benzoyl* derivative,  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{EtBz}\cdot 2\text{HCl}$ . The corresponding *acetyl* derivative has also been prepared. This indicates that there are two replaceable hydrogen atoms in cinchotenine, one probably in a hydroxyl group, and the other in a carboxyl group.

Commercial cinchonine, when oxidised with chromic acid mixture, gave about 3 per cent. of cincholeuponic acid,  $\text{C}_8\text{H}_{13}\text{NO}_4$ . As it was doubtful whether this acid was derived from the cinchonine itself, or

from the impurities, the author has oxidised pure cinchotennine sulphate with chromic acid, and finds that the cincholeuponic acid is one of the products. It thus follows that the acid is a derivative of cinchonine. When the hydrochloride of the acid is suspended in alcohol and the mixture saturated with dry hydrogen chloride, *ethyl cincholeuponate*,  $C_8H_{11}NO_4Et_2.HCl$ , is formed, which melts at  $164-165^\circ$ . This indicates that the acid contains two carboxylic groups. The investigation of this acid, and also of merochinene and other allied substances, is being continued. J. J. S.

**Synthesised Colloïds and Coagulation.** By JOHN W. PICKERING (*J. Physiol.*, 1895, 18, 54-66).—Certain colloid substances, first prepared by Grimaux, exhibit reactions which are very similar to those of proteïds, especially of the globulin class. Two, named *A* and *B*, are prepared by the action of phosphorus pentachloride on metamidobenzoic acid at different temperatures; the colloid *C*, by the action of a current of ammonia at  $170^\circ$  on aspartic anhydride. Each, when dried, resembles dried serum albumin; they dissolve in water, forming pale straw-coloured, opalescent solutions. Each gives the xanthoproteic reaction, and *C* gives a well-marked violet coloration with copper sulphate and potash. In the presence of minute quantities of salts (such as soluble salts of barium, strontium or calcium, sodium chloride, magnesium sulphate, or ammonium chloride), their solutions coagulate on heating to  $75^\circ$ . This is retarded by potassium acetate, sodium sulphate, or excess of glycerol. The passage of a current of carbonic or sulphuric anhydride restores the coagulability destroyed by glycerol. The colloïds are removed from solutions by saturation with magnesium sulphate, ammonium sulphate, or sodium chloride. The separated solid rises to the surface, and readily redissolves on the addition of water. Boiling water renders the colloïds insoluble. Treatment of the insoluble product with ammonia and evaporation in a vacuum regenerates the colloïd, forming a soluble substance which yields all the reactions (including the physiological action immediately to be mentioned) of the original substance.

In the presence of salts, carbonic anhydride precipitates the colloïds, and these redissolve like globulins on substituting a current of air for the carbonic anhydride.

Colloid *C* is digested by pepsin readily, the solution giving the colour reactions of peptone. Colloïd *A* is slightly digestible, *B* is indigestible.

Each when injected intravenously into rabbits causes death by intravascular clotting, 5 to 20 c.c. of a 1.5 per cent. solution being usually fatal. They do not induce coagulation in extravascular (salted) plasma. Full details of these experiments is deferred.

W. D. H.

## Organic Chemistry.

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**Preparation of Ethylic Bromide.** By ADRIAN (*Chem. Centr.*, 1895, i, 20; from *Mon. Sci.*, 1894, [4], 8, 834).—The French *Codex medicamentarius* directs the preparation of pure ethylic bromide by re-distilling the product obtained by heating a mixture of alcohol, sulphuric acid, and potassium bromide. Following the prescribed directions, however, a product is obtained which contains up to 15 per cent. of ether; the author removes the latter by shaking with a small quantity of sulphuric acid which dissolves the ether, and may be separated. On shaking with dilute alkali and distilling with 10 per cent. of sweet almond oil, pure ethylic bromide is obtained.

W. J. P.

**Analogy between the Behaviour of Halogen Alkylenes towards Sodium and like Metals, on the one hand, and towards Mercaptides on the other hand.** By ROBERT OTTO and K. MÜHLE (*J. pr. Chem.*, 1895, [2], 51, 517—521; compare this vol., i, 286).—A table is given illustrating the analogy indicated by the title. From this it is seen that all halogen alkylenes which contain fewer than four carbon atoms, yield the corresponding alkylene, both when they react with sodium or similarly active metals, and when they react with sodium mercaptide; but not all of those which contain a greater number of carbon atoms than four behave in this way with sodium, although they may so behave with sodium mercaptide.

A. G. B.

**Copper and Manganese Cyanides.** By PAUL STRAUS (*Zeit. anorg. Chem.*, 1895, 9, 6—18).—Potassium manganocyanide is best prepared by Christensen's method (*J. pr. Chem.*, 31, 171), but using the following proportions: 15 grams of manganese acetate dissolved in 90 grams of cold water is added to a solution of 25 grams of potassium cyanide in 50 grams of water. A green precipitate is obtained which is redissolved by heating on the water bath with the addition of 25 grams of potassium cyanide. On cooling, the potassium manganocyanide crystallises in beautiful, dark violet, quadratic tablets. It effloresces on exposure to the air, undergoing partial oxidation, is insoluble in water, and, when treated with water, decomposes into potassium cyanide and  $\text{KMn}(\text{CN})_3$ .

Potassium manganicyanide is also prepared, according to Christensen's method, by adding normal manganese phosphate (15 grams) to a solution of potassium cyanide (40 grams) in 150 grams of water. A dark brown precipitate is obtained, which is redissolved by the addition of 20 grams of potassium cyanide. It crystallises in reddish-brown needles, and is stable on exposure to air.

Potassium manganocyanide, when quite free from potassium cyanide, is insoluble in water, but is at once decomposed by it, and the author was unable to obtain ferrimanganocyanide by treating it with ferric chloride. In presence of small quantities of potassium cyanide, the

manganocyanide is soluble, but the blue precipitate obtained with ferric chloride is not pure ferrimanganocyanide.

*Ferrimanganocyanide*,  $\text{Fe}_3\text{Mn}_2(\text{CN})_{12}$ , is obtained by adding a solution of ferrous sulphate to a solution of potassium manganocyanide at a temperature not exceeding  $5^\circ$ , and in an atmosphere of hydrogen. It is a dark blue precipitate, which becomes of a dirty colour on exposure to air, and decomposes with evolution of cyanogen. When heated with soda, it is converted into sodium ferrocyanide with precipitation of manganese and iron. When allowed to remain over sulphuric acid in an atmosphere of hydrogen, it changes to a greenish-black powder, and loses cyanogen.

*Potassium cupromanganocyanide*,  $\text{K}_2\text{Cu}_2\text{Mn}(\text{CN})_6$ , is obtained by adding an aqueous solution of manganese acetate to a solution of potassium copper cyanide,  $(\text{KCN})_6(\text{CuCN})_2$ . It crystallises in white cubes, is stable when damp, but oxidises and turns brown when dried over sulphuric acid. It is insoluble in water, is completely decomposed by boiling with dilute acids, and partially so by alkali carbonates and hydroxides.

*Sodium cupromanganocyanide*, obtained in a similar way to the potassium salt, crystallises in four-sided prisms, and is much more stable and soluble in water than the potassium salt.

*Ammonium cupromanganocyanide* is obtained by treating the sodium salt with ammonium nitrate. It crystallises in six-sided prisms, and is stable on exposure to air.

*Potassium cuprocupricyanide*,  $\text{K}_2\text{Cu}_3(\text{CN})_6$ , is obtained by adding a concentrated solution of copper sulphate to a solution of potassium copper cyanide,  $(\text{KCN})_6(\text{CuCN})_2$ , and heating the mixture for a short time on the water bath. It crystallises in six-sided domes.

The author has attempted to prepare compounds similar to the above from nickel and cobalt salts. When potassium copper cyanide is treated with nickel nitrate a *double salt*, of the composition  $\text{Cu}_2(\text{CN})_2 \cdot 2\text{KCN} \cdot 2[\text{Ni}(\text{CN})_2 \cdot 2\text{KCN}]$ , is obtained. It crystallises in six-sided tablets, and, when treated with water, is decomposed into its constituent salts, the potassium nickel cyanide passing into solution. The corresponding *cobalt salt* is obtained in a similar way, and, when heated with excess of potassium copper cyanide, is converted into potassium cobaltcyanide.

E. C. R.

**Ferrocyanides.** By J. MESSNER (*Zeit. anorg. Chem.*, 1895, 9, 126—143).—The constitution of Prussian blue and Turnbull's blue cannot with certainty be determined either by analysis or by an examination of their decomposition products. Turnbull's blue, which according to the method of its formation is ferrous ferricyanide, is not decomposed by alkalis into ferrous hydroxide and potassium ferricyanide, but into ferric hydroxide and potassium ferrocyanide; that is, it yields the same decomposition products as Prussian blue. The decomposition of the blue with borax, sodium phosphate and the oxides of light and heavy metals, gave no definite results. When treated with cold concentrated hydrochloric acid, the blues are partially dissolved, and the yellow solution, when mixed with water, yields a precipitate of the blue, but decomposition also takes place,

and iron always remains in the solution. Prussian blue treated in this way gave a solution containing ferric oxide together with small quantities of ferrous oxide; Turnbull's blue gave a solution containing ferrous oxide and a small quantity of ferric oxide. The quantitative analysis of the two blues gives no definite result, partly because the theoretical percentage composition [for Prussian blue,  $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$ ; for Turnbull's blue,  $\text{Fe}_3(\text{FeC}_6\text{N}_6)_2$ ] of both is very similar, and partly because the compounds are very difficult to obtain pure. The author gives the results of a number of analyses made with different preparations.

The constitution of Prussian green, for which numerous formulæ have been proposed, is also not determined by its decomposition products. When decomposed by alkalis, it yields ferric hydroxide and potassium ferrocyanide and ferricyanide. Ferricyanides, however, are partially converted by alkalis into ferrocyanides. The analyses of various preparations of Prussian green indicate that it is a ferric ferricyanide,  $\text{Fe}(\text{FeC}_6\text{N}_6)$ . The purest preparation is obtained by saturating a solution of potassium ferricyanide with chlorine, taking care to exclude light, then heating the solution to boiling, allowing it to cool in a current of chlorine, and finally washing out the chlorine with cold water.

Williamson's violet is prepared by careful oxidation of ferropotassium ferrocyanide,  $\text{K}_3\text{Fe}(\text{FeC}_6\text{N}_6)$ . The best method, according to the author, is to use a ferric salt as the oxidising agent. The analyses of various preparations gave widely different results, and the author was unable to determine the composition with certainty. The composition,  $\text{KFe}(\text{FeC}_6\text{N}_6)$ , is based on the formation of the compound by the oxidation of ferropotassium ferrocyanide.

Besides the copper ferrocyanides already described (this vol., i, 405), the author has prepared the following. *Lithium cuproferrocyanide*, obtained by boiling cuprous cyanide with lithium ferrocyanide and lithium sulphite in an atmosphere of hydrogen, crystallises in colourless six-sided prisms. *Lithium cupriferrrocyanide*, obtained by boiling copper ferrocyanide free from alkali with lithium ferrocyanide, crystallises in small, quadratic red plates or brownish-red needles. *Potassium cupriferrrocyanide* is obtained by boiling cuprous cyanide with excess of potassium ferricyanide according to the equation  $\text{CuCN} + 2\text{K}_3(\text{FeC}_6\text{N}_6) = \text{K}_2\text{Cu}(\text{FeC}_6\text{N}_6) + \text{K}_4(\text{FeC}_6\text{N}_6) + \text{CN}$ . It crystallises in brownish-red, quadratic prisms. E. C. R.

### Occurrence of Titanium Cyanonitride in Ferromanganese.

By T. W. HOGG (*Chem. Centr.*, 1895, i, 149; from *Engin. Min. Jour.*, 1893, 664).—Titanium cyanonitride, and sometimes also titanium nitride and carbide, are contained in most samples of ferromanganese. The cyanonitride is obtained by dissolving the ferromanganese in dilute nitric acid, powdering the carbonaceous residue, and washing until only the copper-coloured cyanonitride remains; more than 0.032 per cent. of this substance can never be separated from the alloy. Titanium cyanonitride thus prepared consists of microscopic, brilliant crystals of density 4.1–5.1, and contains 60–80 per cent. of titanium.

W. J. P.

**Carbon Tetrachloride and the Purification of Methylated Alcohol.** By MAXIME CARI-MANTRAND (*Compt. rend.*, 1895, 120, 1063—1064).—The alcohol is mixed with one-fourth its volume of carbon tetrachloride, and afterwards with a sufficient quantity of a saturated solution of sodium chloride (about  $2\frac{1}{2}$  times the original volume) to precipitate the carbon tetrachloride. After repeated vigorous agitation the carbon tetrachloride is separated and retains all the impurities except methylic alcohol and acetone. The saline solution is mixed with sufficient water to reduce the alcoholic strength to  $25^\circ$ , and is then fractionated with a sufficient condensing column to give alcohol of  $96.5^\circ$  to  $97^\circ$  at one distillation. All the product that distils above  $78^\circ$  is pure alcohol.

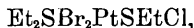
The carbon tetrachloride can be purified by agitating with sulphuric acid at  $66^\circ$  and afterwards washing with water. The salt solution after cooling can be used again. C. H. B.

**Impurities in Ethylic Ether.** By ADRIAN (*Chem. Centr.*, 1895, i, 20; from *Mon. Sci.*, 1894, [4], 8, 835).—Ethylic ether always contains acetaldehyde as an impurity, which can be at once detected and removed by passing dry ammonia into the dried ether when aldehyde-ammonia crystallises out, being insoluble in dry ether; after filtering this off, the ether is shaken with sulphuric acid, and subsequently distilled from potassium carbonate. W. J. P.

**Platinum Compounds of Ethylic Sulphide.** By PETER KLASON (*Ber.*, 1895, 28, 1493—1500).—Blomstrand (*Abstr.*, 1889, 230) has described two isomeric forms of platosethylsulphine chloride, the  $\alpha$ -compound, melting at  $81^\circ$ , and the  $\beta$ -compound, melting at  $106^\circ$ . The author finds that, when pure, the two isomerides melt at the same temperature,  $108^\circ$ , and that they readily pass one into the other. The  $\alpha$ -chloride only reacts slowly with alcoholic silver nitrate solution, whilst the  $\beta$ -chloride appears to react as rapidly as sodium chloride, and a measurement of the electrical conductivity of solutions of the two in dilute alcohol shows that the  $\beta$ -compound is a much better conductor than the  $\alpha$ -chloride. The bromide melts at  $124^\circ$ , and yields the  $\alpha$ -chloride when treated in the cold with silver chloride. It may be prepared from either the  $\alpha$ - or  $\beta$ -chloride by the action of potassium bromide, and is isomorphous with the  $\alpha$ -chloride. The  $\alpha$ -chloride is converted by dry ammonia in chloroform solution into a salt of the formula  $\text{Pt}(\text{NH}_3)_3\text{Et}_2\text{SCL}_2 + \text{H}_2\text{O}$ , which decomposes on heating, leaving a residue containing ammonium platinochloride and the triammonioplatinous chloride of Clève. The  $\beta$ -chloride behaves in a similar manner, yielding an isomeric substance,  $\text{PtEt}_2\text{S}(\text{NH}_3)_3\text{Cl}_2 + \text{H}_2\text{O}$ , which also decomposes when heated, but forms an isomeric triammonioplatinous chloride.

When either of the two chlorides is treated in alcoholic solution with ethylic hydrosulphide or phenylic hydrosulphide, the chlorine atoms are replaced by the thio-radicle, and unstable compounds are formed, which cannot be isolated in the pure state, but rapidly lose ethylic sulphide. In chloroform solution, on the other hand, ethylic hydrosulphide forms the compound, *ethylylsulphideplatosethioethylic*

chloride,  $\text{Et}_2\text{S}\cdot\text{Pt}\cdot\text{SEtCl}$ , which separates from chloroform on the addition of alcohol in yellow crystals melting at  $124^\circ$ . Bromine converts it into *ethylsulphidebromoplatosothioethylic chloride*,



which is an almost insoluble red crystalline powder.

Ethylsulphideplatsothioethylic chloride is converted by ammonia in chloroform solution into *ammonioplatosothioethylamine chloride*,  $\text{EtS}\cdot\text{Pt}(\text{NH}_3)\cdot\text{NH}_3\text{Cl}$ , which crystallises in stellate groups of needles, and gives a crystalline precipitate with potassium chloroplatinite of *ammonioplatosothioethylamine chloroplatinite*.  
A. H.

**Glycerols from Secondary Allylic Alcohols.** By H. FOURNIER (*Bull. Soc. Chim.*, 1895, [3], 13, 121—124).—These can be prepared by Wagner's method, namely, oxidation with 1 per cent. permanganate, and are yellowish, viscid liquids, soluble in water, alcohol, and ether. The triacetates are colourless, and much more mobile.

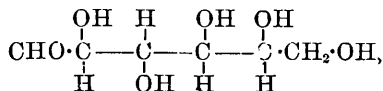
1 : 2 : 4-*Trihydroxyhexane*,  $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$ , from ethylallylcarbinol, boils at  $190\text{--}192^\circ$  (30 mm.); the *triacetate* boils at  $168\text{--}169^\circ$  (20 mm.), or at  $273\text{--}276^\circ$  (atmos.); and has a sp. gr. = 1.086 at  $21^\circ$ .

*Trihydroxyisheptane*,  $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , from isopropylallylcarbinol, boils at  $194\text{--}197^\circ$  (30 mm.); the *triacetate* boils at  $176\text{--}180^\circ$  (20 mm.), or at  $276\text{--}280^\circ$  (atmos.), and has sp. gr. = 1.071 at  $24^\circ$ .

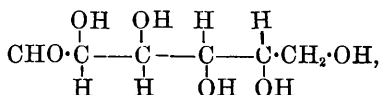
*Trihydroxyisooctane*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , from isobutylallylcarbinol, boils at  $198\text{--}200^\circ$  (30 mm.); it solidifies in a mixture of solid carbonic anhydride and ether, but melts again at about  $0^\circ$ , and not at  $50^\circ$ , as stated by Wagner (*Abstr.*, 1894, i, 563); the *triacetate* boils at  $179\text{--}180^\circ$  (20 mm.), or at  $288\text{--}290^\circ$  (atmos.), but in the latter case decomposes slightly; sp. gr. = 1.049 at  $24^\circ$ .

*Trihydroxyphenylbutane*,  $\text{CHPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , from phenylallylcarbinol, decomposes when distilled, even under very low pressure; the *triacetate* is a viscid, faintly odorous liquid, boiling at  $221\text{--}222^\circ$  (20 mm.).  
JN. W.

**Nomenclature of Stereoisomerides.** By ROBERT LESPIEAU (*Bull. Soc. Chim.*, 1895, [3], 13, 105—108).—An extension of the Geneva system, in which numbers representing the positions of the groups in the conventional formulæ of stereoisomerides are incorporated in their systematic names. Thus, *d*-glucose,



is hexapentol-2456, 3-al, whilst 1-mannose,



is hexapentol-236, 45-al, the numbers being read from the left to the right of the chain, and the upper and terminal numbers preceding, and being separated by a comma from the lower. Optical isomerides are characterised by identical groups in inverted order; *d*-mannose, for example, is hexapentol-456,23-al (the 6 of the  $\text{CH}_2\cdot\text{OH}$ -group remaining unchanged). When all the groups are on one side of the chain, the comma is placed at the end of the formula, for example, hexapentol 23456-al, (? at the end of the numbers -23456,-al). In compounds which, like the hexitol derived from *d*-glucose and *d*-gulose, are symmetrical as to the terminal groups, the formula may be arranged and numbered in two distinct ways, namely, in the case cited, as hexanehexol-146,235, or -12456,3. Such hidden identities may be detected by adding one set of numbers (not including the terminal numbers) to the other set inverted, when the sum of every pair will be the same; thus, in the above case,  $4235 + 3542 = 7777$ .

JN. W.

*Note by Abstractor.*—Identities concealed by double formulæ would be detected on inspecting the graphic formulæ; a precisely similar difficulty occurs with polysubstituted ring-compounds.

**Constitution of Glucosides and Glucoses.** By LEO MARCHLEWSKI (*Ber.*, 1895, **28**, 1622—1623).—The author defends his view of the constitution of glucose and the glucosides (*Abstr.*, 1894, i, 104) against the criticism of E. Fischer (this vol., i, 438).

C. F. B.

**Molecular Modifications of Glucose.** By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 1060—1062).—Dubrunfaut has shown that freshly prepared solutions of glucose have double the rotatory power possessed by solutions that have been prepared for some time, and has isolated the two forms, one having a rotatory power  $[\alpha]_D = +106^\circ$ , and the other  $[\alpha]_D = +52^\circ$ . The author distinguishes the former as  $\alpha$ -glucose, and the latter as  $\beta$ -glucose, and he has obtained a third modification,  $\gamma$ -glucose, the rotatory power of which is only  $[\alpha]_D = +22\cdot50^\circ$ .

*$\alpha$ -Glucose* is the form in which glucose always crystallises from cold water, and, under certain conditions, from alcohol; when dissolved in water, it changes into  $\beta$ -glucose in a few minutes if boiled, in seven or eight hours at  $15^\circ$ , and in more than 30 hours at  $0^\circ$ ; but the change takes place immediately in the cold if 1 per cent. of potassium hydroxide is added. In alcoholic solutions, the change is less rapid the more concentrated the alcohol, and in absolute alcohol only 90 per cent. is converted even after boiling for several hours.

It is obvious that the so-called solubilities of  $\alpha$ -glucose in water or alcohol are really solubilities of  $\beta$ -glucose, or of a mixture of the two.

*$\beta$ -Glucose* is obtained by heating a concentrated solution of very pure glucose on a water bath, with constant agitation, or by adding a fragment of a previous crystallisation to  $\alpha$ -glucose fused at  $100^\circ$ . If the product obtained from hot liquids is dissolved in its own



weight of cold water, gradually mixed with a large quantity of absolute alcohol cooled at  $0^{\circ}$ , and vigorously stirred,  $\beta$ -glucose separates before it has had time to change into  $\alpha$ -glucose.

$\beta$ -Glucose dissolves rapidly in half its weight of water at  $19^{\circ}$ , and after about an hour the liquid begins to deposit  $\alpha$ -glucose. The same change takes place in presence of a quantity of water insufficient to dissolve the glucose, and also partially in a non-saturated alcoholic solution. The solubility of  $\beta$ -glucose in alcohol decreases with the concentration of the alcohol.

$\gamma$ -Glucose is formed in small quantity when amorphous glucose is heated at  $100^{\circ}$ , but the most favourable temperature is  $110^{\circ}$ , and the best plan is to heat at this temperature for seven or eight hours a highly concentrated solution of glucose spread on plates. The crude product is dissolved in its own weight of cold water, decolorised with animal charcoal, and mixed with sufficient absolute alcohol to bring the alcoholic strength to  $90^{\circ}$  or  $95^{\circ}$ , according to the quantity of  $\gamma$ -glucose present, as shown by the polarimeter; if the solution is then vigorously stirred,  $\gamma$ -glucose separates. The treatment is repeated if necessary.

$\gamma$ -Glucose changes completely into  $\beta$ -glucose under the same conditions as  $\alpha$ -glucose, and in about the same time. It dissolves immediately in 0.75 times its own weight of water at  $19^{\circ}$ . The action of alcohol is similar, and if solutions of any of the three glucoses in alcohol of the same concentration are heated for a sufficient length of time, the same rotatory power is obtained. The solubility of  $\gamma$ -glucose in alcohol of various concentrations is about half that of  $\beta$ -glucose.

Cryometric observations show that all three modifications have the same molecular weight.

C. H. B.

**Resolution of Starch by the Action of Oxalic Acid.** By CARL J. LINTNER and GEORG DÜLL (*Ber.*, 1895, **28**, 1522—1531).—In continuation of their investigation of the products of the hydrolysis of starch, the authors have examined the action on it of oxalic acid. Numerous experiments were made with other acids, but this was selected on account of its relatively great activity, the ease with which it can be completely removed, and because, unlike sulphuric acid or hydrochloric acid, it does not cause the formation of reversion products. Saloman's observation that dextrose is readily formed by the action of oxalic acid on starch is confirmed; the best results are obtained as follows. Starch (100 grams) is warmed with water (500 c.c.) containing oxalic acid (2 grams), and the solution heated for an hour under three atmos. pressure. In the following experiments potato starch was always employed.

Amylodextrin appears to be formed, together with compounds of higher molecular weight, almost as soon as the starch has dissolved; the best results were obtained with the following proportions: starch (100 grams), water (400 c.c.), oxalic acid (0.2 gram), heated for  $\frac{1}{2}$  hour under  $2\frac{1}{2}$  atmos. pressure. The compound readily forms spheroidal crystals, consisting of aggregates of needles, but this is no test of purity, as much mother liquor is present; in general pro-

perties, the compound resembles that obtained by the action of diastase (Abstr., 1894, i, 5).

*Erythrodeextrins*.—These were obtained by heating the starch (100 grams) with water at  $65^{\circ}$  (400 c.c.), and 5 per cent. oxalic acid solution (8 c.c.) for one hour under 1.5 atmos. pressure; the product, after treatment with calcium carbonate, gave a reddish-brown iodine reaction; it was evaporated and fractionally precipitated with alcohol; eventually the following products were obtained. *Erythrodeextrin I* ( $C_{12}H_{20}O_{10}$ )<sub>18</sub>, H<sub>2</sub>O,  $[\alpha]_D = 196^{\circ}$ , R = about 3 per cent. (M); iodine reaction, with dilute solution, reddish-violet; forms spheroidal crystals, is sparingly soluble in alcohol (60 per cent.), and probably identical with the compound formed by the action of diastase. *Erythrodeextrin II $\alpha$*  ( $C_{12}H_{20}O_{10}$ )<sub>9</sub>, H<sub>2</sub>O,  $[\alpha]_D = 194^{\circ}$ , R = about 8 per cent. (M); with dilute iodine solution becomes reddish-brown; with concentrated solution (twice normal) in presence of sulphuric acid a pure blue precipitate is formed (the presence of amylodeextrin causes a blue colour with dilute solutions); this, after filtration and washing with dilute sulphuric acid, dissolves in water, and the colour slowly changes to reddish-brown; the change is accelerated by dilution, and the addition of much water causes the colour to disappear completely. The compound is sparingly soluble in cold water, and very readily forms spheroidal crystals. *Erythrodeextrin II $\beta$* , isomeric with the preceding compound, gives a pure reddish-brown coloration with iodine solution, dilute or concentrated, with or without the addition of sulphuric acid; it is insoluble in alcohol (75 per cent.), and was not observed to form spheroidal crystals. The erythrodeextrins II $\alpha$  and II $\beta$ , although not previously observed by the authors, are probably identical with those recently prepared by Nittelmeyer.

*Achroodeextrins*.—Starch (120 grams), water at  $65^{\circ}$  (400 c.c.), and 5 per cent. oxalic acid solution (20 c.c.) are mixed, and heated for one hour under  $1\frac{1}{2}$  atmos. pressure. The osazone test showed that dextrose (21 per cent.), isomaltose (34 per cent.), and dextrin (45 per cent.) were present in the crude product. Maltose could not be detected either in this or in any other experiment. After purification and fractionation of the liquid, two compounds only could be isolated. Achroodeextrin I agrees closely in properties with the corresponding compound previously described (*loc. cit.*), the mol. weight = 1800—2000, specific refractive power =  $192^{\circ}$ . *Achroodeextrin II*, ( $C_{12}H_{20}O_{10}$ )<sub>3</sub>, H<sub>2</sub>O, is crystalline;  $[\alpha]_D = 180^{\circ}$ , Rm = 24. It is extremely difficult to purify, and is probably identical with Mittelmeyer's "primary achroodeextrin."

The following table shows the compounds which have been isolated by the action of oxalic acid and diastase respectively on starch. It is not implied that they are formed in the order mentioned, and the authors consider that the enunciation of any hypotheses relating either to this or to the manner of their formation would be premature until more experimental evidence has been accumulated.

## Compounds formed from starch.

With oxalic acid.	With diastase.
Amylodextrin.	Amylodextrin.
Erythrodestrin I.	Erythrodestrin I.
Erythrodestrin II <sub>a</sub> .	—
Erythrodestrin II <sub>β</sub> .	—
Achroodestrin I.	Achroodestrin I.
Achroodestrin II.	Achroodestrin II.
Isomaltose.	Isomaltose.
—	Maltose.
Dextrose.	—

J. B. T.

**New Type of Lignocellulose.** By W. C. HANCOCK and O. W. DAHL (*Ber.*, 1895, **28**, 1558—1563).—The stem of *Aeschynomene Aspera* is composed of a lignocellulose which differs in some respects from all other members of this class which have yet been described. In composition, behaviour to alkaline agents, absorption of chlorine, &c., it appears to act as a typical lignocellulose. It, however, does not give the characteristic yellow coloration with aniline which is usually given by the lignocelluloses, and is therefore free (except in isolated cells which do give the coloration) from the compounds of aldehyde- or quinone-like character which generally accompany lignocellulose. It, moreover, does not give the phloroglucinol reaction for the pentosanes, although it yields furfuraldehyde when treated by the method of Flint and Tollens. The reaction with iodine and hydriodic acid resembles that of cellulose, a deep blue colour being produced.

A. H.

**Reduction of Hexamethylenetetramine to Trimethylamine.**

By MARCEL DELEPINE (*Bull. Soc. Chim.*, 1895, [3], **13**, 135—140).—Hexamethylenamine is reduced by zinc dust and acetic acid, not to ammonia and methylamine, as stated by Trillat and Fayollat (*Abstr.*, 1894, i, 64), but to ammonia and trimethylamine, and the formation of the triamine takes place equally well under the conditions described by those authors as when the pure hexamine is used. The trimethylamine was characterised by means of its bismuthiodide, methiodide, and platinochloride.

These results confirm the author's formula for hexamethylene-tetramine (this vol., i, 327), from which, as each of the nitrogen atoms is in direct combination with three carbon atoms, the formation of trimethylamine might have been predicted.

JN. W.

**Glucosamine. A Reply.** By ERNST WINTERSTEIN (*Ber.*, 1895, **28**, 1372—1374; compare this vol., i, 80).—A reply to E. Gilson's criticisms (this vol., i, 323) on the author's work on the isolation of glucosamine hydrochloride from the decomposition products of "fungus cellulose."

J. J. S.

**Diazomethane.** By HANS V. PECHMANN (*Ber.*, 1895, **28**, 1624—1628).—Diazomethane may be used in the preparation of methylic derivatives, addition of CH<sub>2</sub> taking place whilst nitrogen is

evolved. Its action on phenol, for example, is represented by the equation  $C_6H_5 \cdot OH + CH_2N_2 = C_6H_5 \cdot OCH_3 + N_2$  (compare this vol., i, 328). The action takes place at the ordinary temperature, and is thus likely to be useful in determining the constitution of compounds that react in tautomeric forms. It is brought about by mixing an ethereal solution of diazomethane with the substance to be investigated, the latter in alcoholic solution when necessary.

2-Pyridone yields only the oxygen ether,  $C_5NH_4 \cdot OMe$  [ $OMe = 2$ ], and hence probably exists in the form  $C_5NH_4 \cdot OH$  rather than  $C_5(NH)H_4 \cdot O$ .

Commercial pyrazolone yields mainly an oxygen-ether, Knorr's 5 : 3 : 1-methoxymethylphenylpyrazole (this vol., i, 397), together with a trace of the nitrogen ether, antipyrine. Pyrazolone itself has therefore probably the constitution  $NPh < \begin{array}{c} N \\ \parallel \\ C(OH) \cdot CH \end{array} \begin{array}{c} Me \\ | \\ Me \end{array}$ .

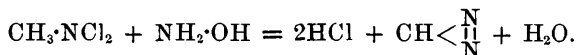
Ethyl acetoacetate yields ethyl  $\beta$ -methoxycrotonate, probably the *cis*-modification, for it boils at  $186-190^\circ$  under 725 mm. pressure, about  $15^\circ$  higher than the (probably *trans*-) compound prepared by Enke (Abstr., 1890, 865). It yields the same methoxycrotonic acid when hydrolysed as does Enke's compound; but ethyl acetoacetate only reacts very slowly with diazomethane, and hence probably exists but to a slight extent as  $OH \cdot CMe \cdot CH \cdot COOEt$ , the greater part being  $CMeO \cdot CH_2 \cdot COOEt$ .

Ethyl malonate does not react with diazomethane in ethereal solution at the ordinary temperature. C. F. B.

**New Synthesis of Diazomethane.** By EUGEN BAMBERGER and EDM. RENAULD (*Ber.*, 1895, 28, 1682—1685).—Diazomethane, which is the anhydride of the hypothetical isodiazomethane hydroxide,  $Me \cdot N : N \cdot OH$ , may be prepared in an analogous manner to isodiazo-benzene, which is formed by the action of hydroxylamine on nitroso-benzene (this vol., i, 459). Nitrosomethane is unknown, but the analogous dichloromethylamine,  $NMeCl_2$ , is readily obtained in quantity by the action of bleaching powder on methylamine hydrochloride; it boils at  $58-60^\circ$ . When heated with water, it explodes violently forming hydrogen cyanide, a similar explosion taking place when a flame is brought near the mouth of a vessel in which the two compounds are warmed.

To prepare diazomethane, dried hydroxylamine hydrochloride is dissolved in methylic alcohol, mixed with the requisite quantity of sodium methoxide also dissolved in methylic alcohol, and a solution of dichloromethylamine in absolute ether gradually added. An ethereal solution of diazomethane distils over, and is condensed in receivers cooled with ice; the solution has all the properties described by v. Pechmann (this vol., i, 328). The yield is not so good as by v. Pechmann's method, but the new synthesis forms a quick and convenient method of obtaining the substance in small quantities.

The reaction by which it is formed is represented by the equation



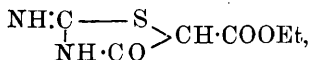
As it is formed by a reaction which yields isodiazobenzene derivatives, the author thinks it probable that this, as well as the aliphatic diazo-derivatives described by Curtius, are also isodiazobenzene derivatives, the supposition being strengthened by the stability of the compounds, and their inability to form colouring matters with phenols and aromatic bases.

H. G. C.

**Nitrosopropylacetamide.** By FELIX CHANCEL (*Bull. Soc. Chim.*, 1895, [3], 13, 125—126).—*Nitrosopropylacetamide*,  $\text{NacPr}^{\text{a}}\text{NO}$ , obtained by the action of nitrous acid on propylacetamide, is a mobile, yellowish, or, in thick layers, rose-coloured, liquid, having a pleasant, ethereal odour. Sp. gr. = 1.035 at 15°. It is almost insoluble in water, and at 100°, either alone or in presence of water, is decomposed into nitrogen and propylenic acetate, together with some propylene and acetic acid resulting from the decomposition of the latter.

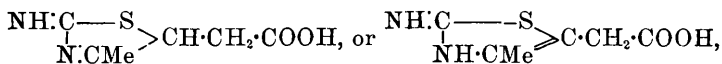
JN. W.

**Action of Thiocarbamide on Ethylic Bromomalonate, Bromolevulinic acid, and Dibromolevulinic acid.** By MAX CONRAD and L. SCHMIDT (*Annalen*, 1895, 285, 203—211; compare Tambach, this vol., i, 13).—*Ethylic thiohydantoïncarboxylate*,



is obtained by adding a concentrated aqueous solution of thiocarbamide to ethylic bromomalonate; it is insoluble in ether, but dissolves readily in boiling alcohol, and undergoes decomposition when treated with boiling water. It becomes brown at 165°, and melts evolving gas at 175°; with ferric chloride, the aqueous solution develops a dark-blue coloration, which is destroyed on heating the liquid, and does not reappear at the ordinary temperature. On boiling a solution of ethylic thiohydantoïncarboxylate in hydrochloric acid, carbonic anhydride is liberated and thiohydantoin is formed, and the same change is effected by sodium hydroxide at ordinary temperatures and also by hot barium hydroxide. Sodium ethoxide gives rise to a gelatinous substance, which probably consists of the sodium compound.

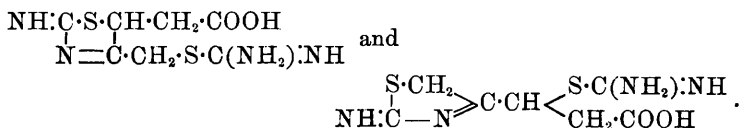
*α-Methyl-μ-amidothiazole-β-acetic acid*,



is prepared by triturating, in contact with water, a mixture of thiocarbamide and bromolevulinic acid in molecular proportion; a solution is obtained, which after 24 hours is neutralised with sodium hydrogen carbonate. It crystallises from water in slender, lustrous prisms, and melts at 259—260°, evolving gas; the aqueous solution has an acid reaction, and decomposes carbonates when heated. The compound dissolves in boiling hydrochloric acid, which, on cooling, deposits the *hydrochloride* in colourless plates; this salt does not yield a precipitate with platinum tetrachloride. The *barium* salt is amorphous, and treatment with excess of hot barium hydroxide effects decomposition,

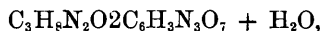
barium sulphide and barium carbonate being formed; a neutral solution of the barium salt forms a green precipitate with copper acetate, whilst silver nitrate gives rise to a white precipitate which becomes black when heated, owing to the formation of silver sulphide. The *ethylic* salt is obtained by mixing alcoholic solutions of thiocarbamide and ethylic bromolevulinate; it separates from alcohol in small, yellowish crystals, and melts at 123°. The *platinochloride* is obtained by dissolving the ethylic salt in cold hydrochloric acid and treating the solution with platinum tetrachloride; it is a yellow crystalline substance. Ammonia and hot hydrochloric acid hydrolyse the ethylic salt, forming the acid and the hydrochloride respectively.

When a mixture of dibromolevulinic acid and thiocarbamide (2 mols.) is triturated in contact with a small quantity of water, a compound is formed having the constitution represented by one of the formulæ



It melts and becomes brown at 175–176°, evolution of gas taking place at this temperature. The formation of this compound is in agreement with the constitutional formula for dibromolevulinic acid put forward by Wolff (Abstr., 1893, i, 689). M. O. F.

**Preparation of Diamidoacetone.** By GEORG KALISCHER (*Ber.*, 1895, 28, 1519–1522).—Diisonitrosoacetone, prepared from acetone-dicarboxylic acid, when reduced by means of stannous chloride in hydrochloric acid solution, yields *diamidoacetone stannochloride*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2\cdot 2\text{HCl}\cdot\text{SnCl}_2$ , which is crystalline and melts at 203°, after previously blackening. The yield is 66 per cent. of the theoretical. The hydrochloride is readily obtained by the action of hydrogen sulphide on the preceding compound, but its complete purification is difficult on account of its solubility; it crystallises with  $1\text{H}_2\text{O}$ , not  $1\frac{1}{2}\text{H}_2\text{O}$ , as Rügheimer states. The *picrate*,



crystallises in lustrous, long, yellow needles, which char at about 180° without melting. When warmed with Fehling's solution, diamidoacetone hydrochloride gives a dark brown precipitate, which is almost black when dry; it contains about 55 per cent. of copper, and yields water and ammonia when heated. Attempts to prepare dihydroxyacetone by the action of nitrous acid on diamidoacetone hydrochloride were not very successful, as the compound could not be completely purified, its presence was recognised by the formation of the osazone which melted at about 170°. J. B. T.

**Action of Hypochlorous acid on Bisubstituted Acetylene Hydrocarbons.** By AL. FAWORSKY and in part by K. DESBOUT (*J. pr. Chem.*, 1895, [2], 51, 533–563).—When hypochlorous acid

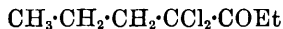
(3 per cent.) is added gradually and in small portions to methyl ethyl ketone, both being at  $0^{\circ}$ , a heavy oil separates. The bulk of this oil distils at  $55-58^{\circ}$  at 20 mm. pressure, and proves to be *methyl  $\alpha$ -dichloropropyl ketone*,  $\text{CEtCl}_2\cdot\text{COMe}$ ; it is a yellowish liquid, boils at  $138^{\circ}$  (756 mm.), and has sp. gr. = 1.19519 at  $0^{\circ}$ . Its constitution is confirmed by the fact that, when treated with hydroxylamine it yields the same dioxime as was obtained by Schramm from isonitrosomethyl ethyl ketone and hydroxylamine ("methylpropylacetoximic acid," Abstr., 1883, 590). The behaviour of this dichloroketone with potassium carbonate has already been described (Abstr., 1893, i, 391). A small fraction of the crude oil from which the dichloroketone is distilled boils between  $108^{\circ}$  and  $112^{\circ}$ , and appears to be  $\alpha$ -dichlorobutaldehyde.

The reaction between methylpropylacetylene and hypochlorous acid yields *methyl  $\alpha$ -dichlorobutyl ketone*,  $\text{CPr}^{\alpha}\text{Cl}_2\cdot\text{COMe}$ , which is a yellowish liquid, boils at  $162-164^{\circ}$  (765 mm.), and has a sp. gr. = 1.14695 (at  $0^{\circ}$ ). With hydroxylamine, it yields Schramm's methylpropylglyoxime (Abstr., 1884, 51). This dichloroketone also yields a quinone and two unsaturated acids when heated with a 10 per cent. solution of potassium carbonate (compare Abstr., 1893, i, 391); these are probably diethyldimethylquinone,  $\alpha$ -propylacrylic acid, and  $\alpha$ -methyl- $\beta$ -ethylacrylic acid respectively, but none of these could be isolated in a pure condition.

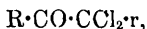
Dimethylacetylene and hypochlorous acid yield *methyl  $\alpha$ -dichloroethyl ketone*,  $\text{CMeCl}_2\cdot\text{COMe}$ , which boils at  $113-114^{\circ}$ , and has a sp. gr. = 1.2217 at  $0^{\circ}$ . Diacetyldioxime was obtained by treating the dichloroketone with hydroxylamine. D  m  tre-Vladesco has prepared a dichlorinated methyl ethyl ketone (Abstr., 1892, 424) which boils at  $165^{\circ}$ , and to which he ascribes the formula given above; the authors have attempted to prepare diacetyldioxime from Vladesco's compound, but without success; they therefore conclude that Vladesco's dichloroketone is the symmetrical derivative.

Asymmetrical dichloroacetone yields acrylic acid when heated with 10 per cent. potassium carbonate solution, so that it may now be regarded as established that, by this treatment, 1 : 1-dichloro-2-ketones of the type  $\text{R}'\cdot\text{CO}\cdot\text{CHCl}_2$  yield acids of the type  $\text{R}''\cdot\text{CH}\cdot\text{COOH}$ , whilst 3 : 3-dichloro-2-ketones of the type  $\text{R}'\cdot\text{CCl}_2\cdot\text{CO}\cdot\text{CH}_3$  yield acids of the type  $\text{R}''\cdot\text{CR}'\cdot\text{COOH}$ .

From ethylpropylacetylene and hypochlorous acid, a dichlorinated ketone is obtained which yields a dioxime (m. p.  $129^{\circ}$ ), and must, therefore, contain the group  $\text{CO}\cdot\text{CCl}_2$ , but whether it be



or  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CCl}_2\text{Et}$  remains unsettled; it boils about  $174^{\circ}$ , and its sp. gr. at  $0^{\circ}$  is 1.1176. This dichloroketone also yields substituted acrylic acids when heated with 10 per cent. potassium carbonate, and since it contains an alkyl group in place of the methyl group of the foregoing ketones, it may be claimed that in this paper it is established that hydrocarbons of the type  $\text{R}\cdot\text{C}::\text{r}$  yield, when treated with hypochlorous acid, dichloroketones of the type



and that these, on treatment with potassium carbonate solution, yield acids of the type  $R''\cdot Cr'\cdot COOH$  or  $r''\cdot cR'\cdot COOH$ . A. G. B.

**Constitution of Isonitrosoketones.** By GEORG KALISCHER (*Ber.*, 1895, **28**, 1513—1519).—The reduction products of isonitroso-propyl methyl ketone,  $COMe\cdot CEt\cdot NOH$ , have been previously described by Gabriel and his students (*Abstr.*, 1893, i, 734; 1894, i, 355). The compounds are indistinguishable in appearance from those obtained by the reduction of Claisen and Manasse's isonitrosoketone,  $COPr\cdot CH\cdot NOH$  (*Abstr.*, 1889, 584), and the melting points are shown to be practically identical. The former yields dimethyldiethylpyrazine, if the formula of the latter is correct it should yield dipropylpyrazine. Dimethyldiethylpyrazine, when completely oxidised with potassium permanganate, yields a tetrabasic acid which could not be purified; when more cautiously oxidised, dimethylpyrazinedicarboxylic acid,  $N<\overset{CMe\cdot C(COOH)}{C(COOH)\cdot CMe}>N$ , is formed; it has been previously prepared by Weengel from ethylic isonitrosoacetate. As dipropylpyrazine could not yield this acid, the isonitrosoketones must be identical, and have the formula  $COMe\cdot CEt\cdot NOH$ . By the action of amylic nitrite and hydrochloric acid on ethyl methyl ketone, an isonitroso-derivative is formed which melts at  $74^\circ$ , and crystallises in slender, colourless needles; the compound from ethylic methylacetate melts at  $73-75^\circ$ ; these are also doubtless identical, and have the formula  $COMe\cdot CMe\cdot NOH$ . Fileti and Ponzio's investigation of isonitroso-nonyl methyl ketone,  $COMe\cdot C(C_8H_{17})\cdot NOH$ , confirms this, and it appears to be a rule that by the action of amylic nitrite and hydrochloric acid on ketones of the formula  $COMe\cdot CH_2R$ , the methylene, and not the methyl, group reacts.

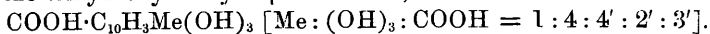
J. B. T.

**Diacetylacetone.** By FRANZ FEIST and HANS BELART (*Ber.*, 1895, **28**, 1817—1829).—Diacetylacetone,  $CO(CH_2\cdot CMeO)_2$ , is best prepared by treating the compound  $C_7H_5O_3Cl + 3H_2O$  (Collie, *Trans.*, 1891, 619) with concentrated baryta water, adding to the yellow barium xantho-salt (*Abstr.*, 1889, 957), thus obtained, cold, moderately concentrated hydrochloric acid, and extracting with ether. It reacts with hydroxylamine much in the same way as with phenylhydrazine (*Annalen*, **257**, 278, 292).

*Diacetylacetonedioxime*,  $C_7H_{10}O(NOH)_2$ , crystallises in needles, and melts at  $68.5^\circ$ ; the *hydrochloride* in white needles, which melt at  $132^\circ$ . The latter is converted by moderately concentrated aqueous soda into the *anhydride* of the dioxime,  $C_7H_{10}N_2O_2$ ; this crystallises in yellow needles, and melts, decomposing with a slight explosion, at  $242.5^\circ$ ; it may also be obtained by heating the dioxime at  $120-125^\circ$  in a test-tube. The action of hydrogen cyanide on diacetylacetone gave no definite result. Phosphorus pentachloride removes water, dimethylpyrone being formed. By treating diacetylacetone (1 mol.) with acetic chloride (rather more than 2 mols.) in the cold, white plates, melting at  $44^\circ$ , were obtained; these probably consist of the *diacetyl derivative*. By heating a mixture of diacetylacetone (1 mol.), benzoic chloride (2 mols.), and sodium ethoxide (2 mols.), a di-



*benzoyl derivative* was obtained; it crystallises in yellow needles, melts at  $55^{\circ}$ , and dissolves in alkalis. When a crude sample of this dibenzoyl derivative was distilled, acetic acid, ethylic benzoate, benzoic chloride, and benzoylacetone were obtained, together with a substance,  $C_{14}H_{14}O_3$ , which crystallises in white needles. Diazobenzene chloride yields, with diacetylacetone, a compound which, probably, has the constitution  $CO[CH(N_2Ph) \cdot CO \cdot CH \cdot N_2Ph]_2$ ; it crystallises in dark reddish-brown needles, and melts at  $152^{\circ}$ . When diacetylacetone is boiled with ethylic acetoacetate in benzene solution, in the presence of solid sodium ethoxide, a small quantity of a neutral substance,  $C_{13}H_{14}O_3$ , is obtained, together with an acid,  $C_{11}H_{14}O_5$ ; they both crystallise in yellow needles, and melt respectively at  $170^{\circ}$  and  $197^{\circ}$ . The second substance is the carboxylic acid of the first, and is also formed, although in smaller amount, when ethylic acetate is used instead of the acetoacetate; it is possibly an ethoxy-derivative formed by the substitution of ethyl for one of the hydroxyl hydrogens in the trihydroxymethylnaphthoic acid,



C. F. B.

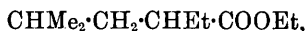
**Conversion of Ketones into  $\alpha$ -Diketones.** By MICHELE FILETTI and GIACOMO PONZIO (*J. pr. Chem.*, 1895, [2], **51**, 498—510, and *Gazzetta*, 1895, **25**, i, 233—245; compare this vol., i, 15.)—By the oxidation of methyl ethyl ketone with nitric acid (sp. gr., 1.38), dimethyl diketone, acetic acid, ammonia and dinitroethane are produced; methyl propyl ketone yields methyl ethyl diketone and dinitropropane, methyl butyl ketone gives methyl propyl diketone and dinitrobutane, whilst methyl hexyl ketone yields methyl amyl diketone, dinitrohexane, and caproic acid. Directions are given for the best method of conducting the oxidation, and the dioximes of the diketones, obtained incidentally as a means of isolating the diketones, are described. *Methyl amyl diketone dioxime*, which crystallises in lustrous prisms and melts at  $170^{\circ}$ , is the only one of these which has not been previously prepared.

A. G. B.

**Formation of Ethereal Salts.** By RUDOLF WEGSCHEIDER (*Ber.*, 1895, **28**, 1468—1474; compare this vol., i, 420).—The author discusses the difference between the views held by Meyer on this question and those previously put forward by himself. He considers that etherification by hydrogen chloride and an alcohol, and hydrolysis are both preceded by the formation of additive compounds, whilst etherification by the action of an alkyl iodide and a silver salt is effected by a direct exchange between the atom of the metal and the alkyl group. Meyer on the other hand refers the difference in the behaviour of the free acid and the silver salt to the different amount of space occupied by the atoms of silver and hydrogen. In considering the effect of neighbouring groups, the author considers that the important point is the volume of the element or group in question, whilst Meyer attaches most importance to its weight.

A. H.

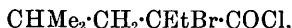
**An Octylic (Ethylmethylvaleric or Ethylisobutylic) Acid.** By PHILIPPE A. GUYE and J. JEANPRÉTRE (*Bull. Soc. Chim.*, 1895, [3], **13**, 182—185).—*Ethyl ethylisobutylic acetate*,



prepared from ethylic acetoacetate by the well known synthetical method, boils at 230—233°; sp. gr. = 0.954 at 15°. The free *acid* boils at 219—220° (729 mm.); sp. gr. = 0.906 at 15°. The *chloride* boils at 165—172°. The *anilide* crystallises in characteristic, thin, flat needles, and melts at 77—78°; it is soluble in the usual menstrua. The intermediate product, *ethylic isobutylacetoacetate*,



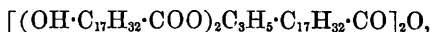
boils at 215—220°. *Ethylisobutylbromacetic chloride*,



prepared by brominating the above chloride, has a sharp, disagreeable odour, and boils at 220—240°. An additive product with 1 mol. of bromine appears to be formed in the first instance, as hydrogen bromide is not disengaged at 100°, even after 2 or 3 hours heating, although the colour of the bromine disappears. At a higher temperature, hydrogen bromide is freely evolved, and the bromacetic chloride distils over. *Ethylic ethylisobutylbromacetate*, prepared from the chloride in the usual manner, boils at 160—165° (80—100 mm.).

JN. W.

**Triricinolein.** By PAUL JUILLARD (*Bull. Soc. Chim.*, 1895, [3], 13, 240—246).—When triricinolein is boiled with toluene, either alone or in presence of zinc chloride, it condenses to various ethers, such as that represented by the formula,



which differ from it in their sparing solubility in alcohol and light petroleum. On account of the slight differences in their composition, their formulæ were established by cryoscopic determinations, both on the substances themselves, and on the mixtures of acids, such as ricinoleic and diricinic acids resulting from them by hydrolysis. They are all oily liquids.

Triricinolein can be synthetised by heating ricinoleic acid with glycerol at 120—230°, unchanged glycerol and acid being dissolved out with water and light petroleum. The product is identical in every respect with that from castor oil. When, however, the parent substances are heated together under the conditions followed by Berthelot in synthetising the palmitins, condensation products of mono- and di-ricinolein are formed, the simplest of which is isomeric with triricinolein, and has the formula,



The ricinoleic acid prepared by Krafft's method is not pure. The pure acid is best obtained from its barium salt after repeated recrystallisation of the latter from alcohol. It melts at 4—5°.

JN. W.

**Natural Dihydroxystearic Acid.** By PAUL JUILLARD (*Bull. Soc. Chim.*, 1895, [3], 13, 238—240).—Castor oil contains, besides ricinoleic and stearic acids, a dihydroxystearic acid isomeric with that

from Turkey red oil (this vol., i, 82), the crude ricinoleic acid obtained by hydrolysis of the oil depositing, when kept for some days at a temperature below  $12^{\circ}$ , a white, crystalline magma of a mixture of stearic acid and the new acid. After purification by pressure, and crystallisation from alcohol, the stearic acid is dissolved out with toluene, and the hydroxy-acid crystallised from boiling alcohol. The yield is about 1 per cent.

*Dihydroxystearic acid*,  $C_{18}H_{36}O_4$ , the molecular weight of which was determined by the cryoscopic method, is insoluble in ether, light petroleum and benzene, only sparingly soluble in toluene, but freely in boiling alcohol and acetic acid. It melts at  $141-143^{\circ}$ . It does not absorb iodine, and is reduced to ordinary stearic acid by hydriodic acid and red phosphorus at  $180^{\circ}$ , or by zinc and acetic acid. It is a monobasic acid. The *potassium*, *sodium*, and *barium* salts are normal. The *methyl* salt crystallises in plates, and melts at  $106-108^{\circ}$ ; the *ethyl* salt resembles it and melts at  $104-106^{\circ}$ .

When heated in a stream of dry carbonic anhydride at  $220^{\circ}$  for eight hours, dihydroxystearic acid is converted into a viscous, feebly acid oil, soluble in ether and insoluble in alcohol; probably a *condensation product* analogous to the ricinoricinic acids; the molecular weight, determined by the cryoscopic method, points to the condensation of 4 mols. of the original acid with elimination of 3 mols. of water. By prolonged boiling with alcoholic potash, the product is gradually hydrolysed with formation of the original acid. A second oily condensation product, obtained by heating the dihydroxy-acid with concentrated hydrochloric acid at  $180^{\circ}$ , or with zinc chloride in toluene solution, is probably a mixture of a dibasic, *dihydroxy-acid*,  $[C_{17}H_{33}(OH) \cdot COOH]_2O$ , and the corresponding monobasic *lactone*; it is soluble in the usual organic menstrua, and has a molecular weight, as determined by the cryoscopic method, of 507. JN. W.

**Maize Meal Fat.** By F. ROKITANSKI (*Chem. Centr.*, 1895, i, 22; from *Pharm. Zeit. f. Russland*, 1894, 33, 712-713).—An aromatic, yellow, neutral oil, of density 0.836, is extracted by light petroleum from the small yellow Italian maize grown in Southern Russia; it gives the elaidin reaction and has a Hübl's iodine number of 75.8 and a Reichert-Meissl number of 0.87. Formic acid was detected, and capronic, caprylic and capric acids also are probably present; the solid fatty acids contain oleic acid and hydroxy-acids, as is shown by their iodine number (97.8), their lead salts, and their behaviour on acetylation, and yield a mixture of ethylic salts boiling at  $240-242^{\circ}$ . On oxidising the acid regenerated from this salt, a *tetrahydroxystearic acid* melting at  $168-170^{\circ}$ , and probably also a *dihydroxystearic acid*, are obtained. The readiness with which maize meal becomes rancid is probably due to the presence of linoleic acid.

W. J. P.

**Acetylacetone. Ethylic Acetoacetate.** By RICHARD S. CURTISS (*Amer. Chem. J.*, 1895, 17, 435-443).—The neutral compound obtained by Nef from the reaction between silver acetylacetone and ethylic iodide (*Abstr.*, 1894, i, 31) is shown to be  $\alpha$ -acetyl- $\beta$ -ethoxypropylene; it is a fragrant oil which becomes light green on standing.

The  $\alpha$ -ethylacetylacetone formed at the same time (*loc. cit.*) yields a copper derivative,  $C_{14}H_{22}O_4Cu$ , when shaken with an aqueous solution of copper acetate; it is insoluble in water, but dissolves in most hot organic solvents and in cold chloroform, and crystallises in long, silky, greyish-green needles which become brown at  $205^\circ$  and melt at  $210$ – $212^\circ$ .

Claisen (this vol., i, 62) states that, among other points of difference which he observes between the behaviour of hydroxymethylene compounds and that of ethylic acetoacetate, the hydroxymethylene compounds are converted into ethylic salts by the action of hydrochloric acid and alcohol. The author shows that ethylic acetoacetate is converted by alcohol, alone or in the presence of hydrogen chloride, into ethylic  $\beta$ -ethoxycrotonate; he thus disposes of Claisen's point of difference.

When ethylic  $\beta$ -ethoxycrotonate is treated with bromine (1 mol.) in carbon tetrachloride at  $-10^\circ$ , the ethylic salts of  $\alpha$ - and  $\gamma$ -bromo- $\beta$ -ethoxycrotonic acids are formed, together with those of  $\alpha$ - and  $\gamma$ -bromacetoacetic acids.

Hantzsch and Epprecht (Abstr., 1894, i, 171) have attempted to throw doubt on Nef's experiments, which showed that Duisberg's ethylic bromacetoacetate is a mixture of the ethylic salts of  $\alpha$ - and  $\gamma$ -bromacetoacetic acids (Abstr., 1892, 143). The author has re-examined Duisberg's product, and has isolated the copper salt of ethylic  $\alpha$ -bromacetoacetate from it.

A. G. B.

**Isonitramine and Oxazo-derivatives of Fatty acids.** By WILHELM TRAUBE (*Ber.*, 1895, 28, 1785–1797; compare Abstr., 1894, i, 400, this vol., i, 124).—The isonitramine derivatives of ethylic acetoacetate, previously described by the author, are readily hydrolysed by alkalis with simultaneous elimination of the acetyl group and formation of the corresponding isonitramine fatty acid. These form crystalline salts, but, with the exception of isonitraminephenylpropionic acid, none of the free acids could be obtained in the crystalline condition. On reduction in acid solution, these compounds yield the corresponding amido-acids, whilst in alkaline solution they are converted into hydrazines; hence the two nitrogen atoms must be directly connected together, and one must also be directly combined with carbon. Either of the following constitutional formulæ fulfils these conditions equally well:—



Ethylic isonitramineacetoacetate is best prepared by passing nitric oxide into an alcoholic solution of ethylic acetoacetate (1 mol.) and sodium ethoxide (1 mol.), and, after complete saturation, adding another mol. of sodium ethoxide. The precipitated sodium salt is very susceptible to the action of acids, 70–80 per cent. of the nitrogen being evolved in the free state, whilst acetic and oxalic acids are formed together with ethylic isonitrosoacetoacetate. On treatment with phenylhydrazine, it yields the *hydrazone of ethylic acetoglycollate*,

$\text{N}_2\text{HPh}\cdot\text{CMe}\cdot\text{CH}(\text{OH})\cdot\text{COOEt}$ , which crystallises in rhombic plates melting at  $102^\circ$ . For the preparation of *isonitramineacetic acid*,  $\text{HO}_2\text{N}_2\cdot\text{CH}_2\cdot\text{COOH}$ , the crude solution obtained by the action of nitric oxide on ethylic sodacetoacetate is mixed with the theoretical quantity of soda, and warmed until all the alcohol is driven off; the acid is then precipitated as the lead salt, which is crystalline and insoluble in water. The *calcium* salt,  $\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{Ca} + 2\text{H}_2\text{O}$ , crystallises in well developed prisms which do not lose water at  $180^\circ$ . The *ammonium* salt, which, like all the ammonium salts of these acids, only contains 1 mol. of ammonia, crystallises in colourless plates which melt at  $166\text{--}168^\circ$  and then decompose without explosion; the *barium* salt is granular, and the *silver* salt forms concentric aggregates of needles. The free acid is stable only in solution. *Isonitraminepropionic acid*,  $\text{HO}_2\text{N}_2\cdot\text{CHMe}\cdot\text{COOH}$ , obtained in the same manner from ethylic methylacetoacetate, closely resembles the foregoing compound; its *lead* salt,  $\text{C}_3\text{H}_4\text{N}_2\text{O}_4\text{Pb}$ , is crystalline, and insoluble in water and dilute acetic acid. *Isonitraminebutyric acid*,  $\text{HO}_2\text{N}_2\cdot\text{CHEt}\cdot\text{COOH}$ , prepared from ethylic ethylacetoacetate, is also only known in solution; the *lead* salt is a crystalline, explosive powder; the *barium* salt,  $\text{C}_4\text{H}_6\text{N}_2\text{O}_4\text{Ba}$ , forms crystalline crusts, and the *ammonium* salt concentric aggregates of broad, colourless needles melting and decomposing at  $156\text{--}159^\circ$ . Salts of *isonitraminevaleric acid* have also been prepared. *Isonitraminephenylpropionic acid*,  $\text{HO}_2\text{N}_2\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{COOH}$ , differs from the foregoing compounds, inasmuch as it has been obtained in the crystalline state. It is prepared from ethylic benzylacetoacetate, and forms large, yellowish crystals containing  $2\text{H}_2\text{O}$  which are rapidly removed if it is kept over sulphuric acid. It melts at  $72^\circ$ , and gives Liebermann's reaction; its *ammonium* salt crystallises in plates and melts at  $179^\circ$ .

Ethylic malonate, in presence of sodium ethoxide, absorbs nitric oxide more readily than ethylic acetoacetate does; the product on boiling with the requisite quantity of soda yields a sodium salt having the composition  $\text{N}_2\text{OC}(\text{COONa})_2 + 2\text{H}_2\text{O}$ , which forms lustrous needles and loses its water of crystallisation at  $130\text{--}140^\circ$ . The *barium* salt,  $\text{N}_2\text{OC}(\text{COO})_2\text{Ba}$ , crystallises in lustrous plates and loses its water of crystallisation at  $170^\circ$ ; the *calcium* salt forms prisms, and the *lead* salt a curdy precipitate which gradually becomes crystalline. All the salts are explosive, and the free acid could not be obtained crystalline. This acid contains the elements of 1 mol. water less than the isonitramine malonic acid  $\text{HO}_2\text{N}_2\cdot\text{CH}(\text{COOH})_2$ , whose formation was expected, and it has, therefore, probably the constitution  $\text{ON}_2\cdot\text{C}(\text{COOH})_2$ , and the author proposes for it the name *oxazomalonic acid*. Another possible formula is  $\begin{array}{c} \text{O}-\text{CO} \\ | \\ \text{O}-\text{N}_2 \end{array} > \text{CMe}\cdot\text{COOMe}$ ,

but it is very improbable that a lactone-like substance of this constitution would be formed by the action of boiling alkalis. In addition to oxazomalonic acid, small quantities of isonitramineacetic acid are also formed, and in the case of the substituted ethylic malonates only the isonitramine fatty acids are obtained, no compounds analogous to oxazomalonic acid having yet been prepared.

Benzyl cyanide is acted on by nitric oxide in presence of sodium

ethoxide forming the very unstable *diisonitraminebenzylic cyanide*,  $\text{CPh}(\text{N}_2\text{O}_2\text{H})_2\text{CN}$ , which forms a snow-white, crystalline powder. Its *barium salt*,  $\text{C}_8\text{H}_5\text{N}_5\text{O}_4\text{Ba}$ , is crystalline, and almost insoluble in water, and, like the other salts, is decomposed by acetic acid with formation of isonitrosobenzyl cyanide.

H. G. C.

**Derivatives of Galactonic acid.** By EMIL KOHN (*Monatsh.*, 1895, **16**, 333—343; compare Skraup, *Abstr.*, 1894, i, 15).—When hydrogen chloride is passed through calcium galactate suspended in alcohol, the liquid at first becomes clear, but later a substance of the composition  $(\text{C}_6\text{H}_{11}\text{O}_7\text{Et})_2\text{CaCl}_2$ , separates as a gelatinous mass which soon becomes crystalline. The free *ethyl derivative*, on account of its instability, could not be isolated from this compound, but the *pent-acetyl derivative*,  $\text{CH}_2(\text{OAc})\cdot[\text{CH}\cdot\text{OAc}]_4\cdot\text{COOEt}$ , was formed on acetylation with acetic chloride, or still better, with acetic anhydride. It is crystalline, melts at  $101\text{--}102^\circ$ , and with ammonia yields the *amide of galactonic acid*,  $\text{C}_6\text{H}_{11}\text{O}_6\cdot\text{CONH}_2$ , which at  $172\text{--}173^\circ$  melts with decomposition and evolution of gas. The *anilide of galactonic acid*,  $\text{C}_6\text{H}_{11}\text{O}_6\cdot\text{CONHPh}$ , crystallises from alcohol in bright scales and melts at  $210^\circ$ .

G. T. M.

**Separation and Identification of Alkylated Succinic and Glutaric acids.** By KARL AUWERS (*Annalen*, 1895, **285**, 212—229).—Two general methods for the separation of substituted succinic and glutaric acids are described, namely: (1) treatment with acetic chloride, which converts some acids of this type into the anhydride, leaving others unchanged; (2) distillation in an atmosphere of steam. Reference must be made to the original paper for details of the separation, which are influenced by the composition of the mixture.

Identification of the various acids depends on their more important characteristics; for instance, melting point, volatility, temperature at which elimination of water takes place, crystalline form, solubility, behaviour towards hot hydrochloric acid, electrical conductivity, and behaviour of the anhydrides towards bases. The last-named method of characterisation is carried out by preparing a solution of the anhydride in benzene and treating it with a molecular proportion of an aromatic base dissolved in the same medium; in this way, an anilic acid is obtained which, if derived from a glutaric acid, melts without decomposition, but becomes converted into an anil through elimination of water if the original anhydride is of the succinic type. The anils and anilic acids, which find useful application in this way, are described in the following abstract.

M. O. F.

**Anilic acids and Anils of Alkylated Succinic and Glutaric acids.** By KARL AUWERS, A. OSWALD, and JOCELYN F. THORPE (*Annalen*, 1895, **285**, 229—239; compare this vol., i, 209).—The general method of preparing the anilic acids consists in mixing benzene solutions of the anhydride and a base; the anils are obtained from the anilic acids by heating them at the melting point, or in the case of those derived from glutaric acid, heating them for a

few minutes at the boiling point under reduced or atmospheric pressure.

The following derivatives have been prepared from dimethylsuccinic acid (high melting point). The *anilic acid* melting at 169°; the *anil* at 126–127°; the *paratolilic acid* at 198°; the *paratolil* at 120°; the  $\beta$ -*naphthilic acid* at 209°; and the  $\beta$ -*naphthil* at 200°.

The anil of dimethylsuccinic acid (low melting point) has been already described (Bischoff and Voit, *Ber.*, 1890, **23**, 643). The *anilic acid* melts at 135–136°; the *paratolilic acid* at 164–165°; the *paratolil* at 153°; the  $\beta$ -*naphthilic acid* at 140°; and the  $\beta$ -*naphthil* at 220°.

M. O. F.

**Trimethylsuccinic acid and the Symmetrical Dimethylglutaric acids.** By KARL AUWERS (*Annalen*, 1895, **285**, 241–284; compare this vol., i, 209; also Bone and Perkin, *Trans.*, 1895, 416).—A preliminary notice of the work has already appeared (*loc. cit.*), and the author's conclusion that trimethylsuccinic acid occurs in one form only, melting at 147°, has been confirmed by Bone and Perkin (*loc. cit.*). The present paper treats the subject in a more detailed manner, and summarises the experimental evidence to which the two following abstracts have reference.

The fumaroid dimethylglutaric acid yields the anhydride less readily than the maleinoid form, and on this circumstance the author bases an argument in favour of v. Baeyer's explanation of the isomerism of dialkylated succinic acids and similar compounds; a view is also put forward which accounts for the preponderance of the maleinoid modification in the mixture of acids obtained from ethylic sodio- $\alpha$ -cyanopropionate and methylenic iodide.

Attention has already been drawn by v. Baeyer to the similarity between hexahydro-derivatives of the benzenedicarboxylic acids and the aliphatic acids containing the same number of carbon atoms between the carboxyl groups (*Abstr.*, 1893, i, 714); the author shows that the resemblance between the symmetrical dimethylglutaric acids and the hexahydroisophthalic acids is not maintained in every particular.

M. O. F.

**Sources of Trimethylsuccinic acid.** By KARL AUWERS and A. OSWALD (*Annalen*, 1895, **285**, 283–309; compare foregoing abstract, also this vol., i, 209, and *Trans.*, 1895, 416).—The paper contains a description of the various methods of obtaining trimethylsuccinic acid. The *lead* and *copper* salts are crystalline, and contain  $\text{H}_2\text{O}$ ; the *imide* crystallises in lustrous needles, and melts at 121°.

M. O. F.

**Symmetrical  $\alpha\alpha$ -Dimethylglutaric acids.** By KARL AUWERS and JOCELYN F. THORPE (*Annalen*, 1895, **285**, 310–339; compare this vol., i, 209).—The authors describe methods for the preparation of the symmetrical dimethylglutaric acids; the main facts have already appeared (*loc. cit.*).

The fumaroid acid crystallises in long prisms belonging to the monosymmetric system,  $a:b:c = 0.4409:1:0.295$ ;  $\beta = 94^\circ 16' 30''$ . The maleinoid modification forms crystals belonging to the asym-

metric system,  $a : b : c = 0.4688 : 1 : -$ ;  $\alpha = 107^\circ 49' 30''$ ,  $\beta = 114^\circ 18'$ ,  $\gamma = 74^\circ 55' 30''$ . The anhydride of these acids forms monosymmetric crystals,  $a : b : c = 0.92547 : 1 : -$ ;  $\beta = 91^\circ 21' 35''$ .

M. O. F.

**Racemism.** By LEO MARCHLEWSKI (*Ber.*, 1895, **28**, 1611—1612).—The author points out that he drew attention to the fact that racemic acid in 10—14 per cent. solution has a smaller specific volume than tartaric acid (*Abstr.*, 1892, 964), before Liebig did, whose work is referred to by Wallach (*Annalen*, **286**, 134) in this connection.

A. H.

**Ethylic Oxalosuccinate.** By WILHELM WISLICENUS and MAX NASSAUER (*Annalen*, 1895, **285**, 1—10; compare *Abstr.*, 1894, i, 323).—Specimens of ethylic oxalosuccinate which have been distilled, invariably contain traces of ethylic ethanetricarboxylate owing to elimination of carbonic oxide (*loc. cit.*); a pure product may be obtained, however, by using potassium carbonate in the manner already described, without submitting the oil to distillation; and when prepared in this way, ethylic oxalosuccinate is almost colourless and odourless.

Unlike the ethylic salts of  $\beta$ -ketonic acids, ethylic oxalosuccinate does not yield a ketone or ketonic acid on hydrolysis; when boiled with dilute sulphuric acid, it yields succinic acid, carbonic anhydride, and oxalic acid, the last-named product being further decomposed into carbonic oxide and formic acid. Aqueous potash and baryta also resolve ethylic oxalosuccinate into oxalic and succinic acids, and the action of water at  $150^\circ$  for six hours effects the same result, the oxalic acid undergoing decomposition into carbonic anhydride and formic acid.

The ethylic salt of isocitric acid,



(Fittig and Miller, *Abstr.*, 1890, 587), is obtained by reducing ethylic oxalosuccinate with sodium amalgam; it is a colourless, odourless and viscous oil, which boils at  $149$ — $150^\circ$  under a pressure of 14 mm. The sodium salt, which is produced at the same time, is extremely soluble in water.

M. O. F.

**Ethylic Dioxalosuccinate.** By WILHELM WISLICENUS and AUGUST BOECKLER (*Annalen*, 1895, **285**, 11—34).—*Ethylic dioxalosuccinate*,  $\text{COOEt} \cdot \text{CO} \cdot \text{CH}(\text{COOEt}) \cdot \text{CH}(\text{COOEt}) \cdot \text{CO} \cdot \text{COOEt}$ , is obtained by the action of sodium ethoxide on a mixture of ethylic oxalate and ethylic succinate dissolved in ether; after several days, the ethereal liquid is agitated with water, and on acidifying the aqueous extract, ethylic dioxalosuccinate is obtained as an oil. The salt combines with phenylhydrazine, hydroxylamine, and ammonia; the alcoholic solution develops a deep reddish-brown coloration with ferric chloride. Carbonic oxide is eliminated from ethylic dioxalosuccinate under the influence of heat, and ethylic ethanetetracarboxylate is formed. The disodium salt is a yellow, hygroscopic substance, which dissolves very readily in water; the aqueous solution is alkaline, and reduces copper acetate and mercuric chloride when



gently heated, an intense red coloration being developed in the case of the latter. When the solution of the disodium salt in cold water is neutralised with dilute sulphuric acid, and allowed to remain for several hours at the ordinary temperature, a yellow, crystalline precipitate is formed, consisting of the *sodium* salt of the lactone of ethylic dioxalosuccinate; the warm, aqueous solution reduces mercuric chloride, copper acetate, and Fehling's solution, a red coloration being developed with the mercuric salt. The *lactone* of ethylic

dioxalosuccinate,  $\text{COOEt}\cdot\overset{\text{COOEt}}{\underset{\text{COOEt}}{\text{C}}}\cdot\overset{\text{COOEt}}{\underset{\text{COOEt}}{\text{C}}}\cdot\text{CH}(\text{COOEt})\text{---CO} > \text{O}$ , is obtained by adding

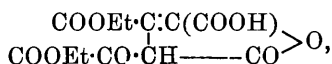
dilute sulphuric acid to an aqueous solution of the sodium salt; it crystallises from alcohol in lustrous needles, and melts at 89—90°. The lactone is acid in character, and with alkalis, alkali carbonates, or sodium acetate, yields solutions from which it is thrown down by sulphuric acid. The alcoholic solution develops a reddish-brown coloration with ferric chloride, and when copper acetate or mercuric chloride is warmed with the solution in aqueous sodium acetate, the metallic salt is reduced. The lactone is decomposed by hot aqueous sodium hydroxide, yielding oxalic and succinic acids; when the ethereal solution is treated with sodium (1 mol.) dissolved in alcohol, the sodium salt is formed, whilst the disodium salt of ethylic dioxalosuccinate is produced if twice this proportion of sodium is employed. The *ammonium* salt of the lactone crystallises in colourless leaflets, and melts at 160°, gas being evolved at this temperature; at 165° water is eliminated, and a *compound* is formed which melts at 220—227°, and when heated with soda-lime yields a vapour which gives the pyrroline reaction. The *phenylhydrazone*,  $\text{COOEt}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CH}(\text{COOEt})\cdot\text{CH}(\text{COOH})\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{COOEt}$ , is obtained by adding phenylhydrazine (2—3 mols.) dissolved in glacial acetic acid, to an alcoholic solution of the lactone; it forms small, colourless crystals, and melts at 138°. It dissolves in aqueous sodium hydroxide, and ferric chloride develops an intense violet coloration with the solution in concentrated sulphuric acid.

When the lactone of ethylic dioxalosuccinate is hydrolysed with aqueous soda (2 mols.), the *disodium* salt of the acid lactone of ethylic

dioxalosuccinate,  $\text{COOEt}\cdot\overset{\text{COONa}}{\underset{\text{COONa}}{\text{C}}}\cdot\overset{\text{COONa}}{\underset{\text{COONa}}{\text{C}}}\cdot\text{CH}(\text{COONa})\text{---CO} > \text{O}$ , is formed; it is

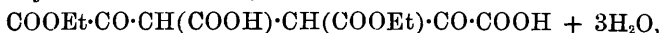
also produced by boiling the alcoholic solution of the disodium salt of ethylic dioxalosuccinate, or on allowing the aqueous solution to remain for several hours at the ordinary temperature. The salt is pale yellow, and insoluble in alcohol, but dissolves readily in water; the aqueous solution is neutral, and yields a white precipitate with solutions of lead acetate and calcium chloride. Barium chloride gives rise to a crystalline precipitate when gently heated; phenylhydrazine acetate produces a yellow, flocculent precipitate, and copper acetate is reduced on application of heat. Mercuric chloride is likewise reduced, the liquid becoming reddish-yellow, the colour being more intense if the solution of the sodium salt is previously heated with aqueous soda.

The *acid lactone* of ethylic dioxalosuccinate,



is prepared from the foregoing disodium salt by treating it with acid, and from the disodium salt of ethylic dioxalosuccinate, by allowing the aqueous solution to become neutral spontaneously, and extracting with ether after the addition of acid. It dissolves readily in water, alcohol, and ether, and crystallises from benzene or chloroform in slender, colourless needles; at 170—171° it melts and evolves gas. The alcoholic solution develops a deep, reddish-brown coloration with ferric chloride, and yields an oil with phenylhydrazine; in its behaviour towards other reagents, it resembles the sodium salt. Boiling aqueous alkalis decompose it into oxalic and succinic acids.

*Diethylic dioxalosuccinate,*



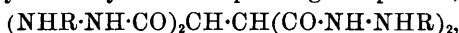
is obtained by the action of cold aqueous soda on the disodium salt of the foregoing acid lactone. It separates from hot water in small, lustrous, rhombic crystals, and melts at 90—92°. It reduces copper acetate and Fehling's solution, and in presence of sodium acetate mercuric chloride is also reduced, an intense, blood-red coloration being developed. Ferric chloride does not produce any coloration in the alcoholic solution. The *phenylhydrazone* melts at 160—165°, and the sulphuric acid solution develops a deep violet coloration with ferric chloride. The *barium* salt,  $\text{C}_{12}\text{H}_{12}\text{O}_{10}\text{Ba} + \text{H}_2\text{O}$ , is crystalline. Cold alkalis have no further hydrolytic action on diethylic dioxalosuccinate, which is resolved, however, by hot solutions into oxalic and succinic acids. Elimination of water takes place when diethylic dioxalosuccinate is heated at 120°, the acid lactone (m. p. 170—171°) being formed.

M. O. F.

#### Action of Hydrazines on Ethylic Ethanetetracarboxylate.

By A. SALOMON and E. POHL (*Ber.*, 1895, **28**, 1722—1724).—By the interaction of hydrazine and ethylic ethanetetracarboxylate in dilute alcoholic solution, the dihydrazide,  $\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \\ | \qquad \qquad | \\ \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \end{array}$ , is formed;

this does not crystallise, reduces silver and copper solutions, yields a dark green oxidation product with ferric chloride, dissolves in dilute ammonia, is decomposed by hydrochloric acid, liberates carbonic anhydride from carbonates, and, with concentrated ammonia, yields a reddish-brown compound, which has not yet been investigated. The *barium* and *calcium* salts contain 1 and 2H<sub>2</sub>O respectively, both are at first colourless, but the latter rapidly turns blue. Phenylhydrazine and paratolylhydrazine yield corresponding compounds,



which could not be recrystallised.

J. B. T.

**Ortho-Substitution Products in the Thiophen Series.** By K. KEISER (*Ber.*, 1895, **28**, 1804—1807).—The starting point for the preparation of these derivatives was dimethylthiophen, obtained from

coal-tar xylene. When the dibromo-derivative is mixed with acetic chloride in light petroleum solution and aluminium chloride added, *monobromacetylmethylthiophen*,  $C_4SHMeBrAc$ , melting at  $77^\circ$ , is formed. When acetyldimethylthiophen, in carbon bisulphide solution, is treated with the theoretical quantity of bromine in cooled aqueous solution, a *monobromo-derivative* is formed, the bromine having entered the ring; this compound melts at  $78^\circ$ . In the same way, acetothienon can be made to yield its monobromo-derivative.

*Benzoyldimethylthiophen*,  $C_4SHMe_2Bz$ , was prepared by the action of benzoic chloride on dimethylthiophen; it melts at  $56^\circ$ , and yields a *monobromo-derivative*, which melts at  $78^\circ$ , and forms a colourless *oxime*; this *oxime* does not yield an indoxazen. C. F. B.

**Dimethylthiophen (Thioxen).** By MORITZ KITT (*Ber.*, 1895, 28, 1807—1814).—The dimethylthiophen prepared by Paal (*Abstr.*, 1885, 1205) from phosphorus pentasulphide and acetonylacetone,  $CMeO \cdot CH_2 \cdot CH_2 \cdot CMeO$ , must obviously have the constitution,  $C_4SH_2Me_2$  [ $Me_2 = 2 : 5$ ]. It has been generally thought to be identical with that from coal-tar, but the author has prepared various derivatives of it, and compared them with the corresponding derivatives of coal-tar dimethylthiophen prepared by himself, Keiser (preceding abstract) and Zelinski (*Abstr.*, 1888, 939). These were found to differ in melting point and in other respects; hence coal-tar thioxen cannot have the 2:5-constitution, but must have one of the three isomeric formulæ.

2:3:5-*Dimethylthiophenyl phenyl ketone*,  $C_4SHMe_2 \cdot CPh$ , prepared by the action of benzoic chloride on synthetical 2:5-dimethylthiophen, melts at  $44\text{--}45^\circ$ ; Keiser's preparation, from coal-tar dimethylthiophen, melted at  $50\text{--}51^\circ$ , using the same thermometer. When dissolved in carbon bisulphide and treated with bromine water, it yields a *monobromo-derivative*,  $C_4SBrMe_2 \cdot CPh$ , which melts at  $85^\circ$ ; Keiser's compound melted at  $77^\circ$ . The formation of this compound disproves Marcusson's rule (*Abstr.*, 1894, i, 16), that one is "unable to obtain thiophen derivatives having a halogen or nitro-group in the ortho-position relatively to a CO group." The monobromo-derivative yields a yellowish *oxime*, which melts at  $176\text{--}177^\circ$ , and does not, like the corresponding benzene derivatives, yield an indoxazen; probably the ortho-substituted oximes have a different stereometric configuration in the thiophen and benzene series.

2:3:5-*Dimethylthiophencarboxyl amide*,  $C_4SHMe_2 \cdot CONH_2$ , was prepared by adding aluminium chloride to a solution of 2:5-dimethylthiophen and carbamide chloride in carbon bisulphide; it melts at  $133\text{--}134^\circ$ , and is hydrolysed by alcoholic potash to 2:3:5-*dimethylthiophencarboxylic acid*,  $C_4SHMe_2 \cdot COOH$ , which melts at  $117\text{--}118^\circ$ . The corresponding derivatives of coal-tar thioxen melt at  $119\text{--}120^\circ$ , and  $163\text{--}164^\circ$  (Zelinski,  $115\text{--}116^\circ$  and  $171\text{--}172^\circ$ ). The 2:3:5-acid yields a monobromo-derivative,  $C_4SBrMe_2 \cdot COOH$ , melting at  $188\text{--}189^\circ$ ; this affords another contradiction of Marcusson's rule.

C. F. B.

**Addition of Sulphur to Unsaturated Organic Compounds.** By ARTHUR MICHAEL (*Ber.*, 1895, 28, 1633—1637).—Various unsatu-

rated organic compounds were caused to combine with sulphur by heating them with it in sealed tubes for 20 hours, at temperatures varying between 150—210°. Ethylic fumarate yields a compound,  $S:C_2H_2(COOEt)_2$ ; this is a yellowish oil of unpleasant odour, and boils above 180° under 20 mm. pressure. Methylic and ethylic acetylenedicarboxylates unite with only half as much sulphur, yielding thiophen derivatives,  $S \begin{smallmatrix} \diagup C(COOMe):C \cdot COOMe \\ \diagdown C(COOMe):C \cdot COOMe \end{smallmatrix}$ , &c.; the methylic compound forms colourless prisms, and melts at 126—128°; the ethylic compound is an oil, and boils, with slight decomposition, at 240—250° under 20 mm. pressure. Cinnamene also unites with sulphur, forming a compound  $C_8H_8S$ ; this was obtained in an impure form as a reddish oil, boiling above 180° under 25 mm. pressure.

C. F. B.

**An Acid,  $C_5H_6O_2$ , from Hexachloroketopentene.** By THEODOR ZINCKE (*Ber.*, 1895, 28, 1644—1647).—The acid,  $C_5H_6O_2$ , obtained in small quantity, together with ethylidenepropionic acid (*Abstr.*, 1893, i, 698; this vol., i, 131), when the acid,  $C_4Cl_5COOH$ , formed from hexachloroketopentene by the action of alkalis, is reduced with sodium amalgam, is now shown to be an unsaturated compound, probably containing two double linkings, for it unites with  $2HBr$ , but only with 1 mol. of bromine,  $Br_2$ . *Butinenecarboxylic acid*,  $C_4H_5COOH$ , crystallises in large, colourless, lustrous, monoclinic plates, and melts at 102—103°; the *barium* and *calcium* salts were prepared, the latter crystallising with  $H_2O$ . With bromine, it yields *dibromopentenic acid*,  $C_5H_6Br_2O_2$ , which crystallises in colourless needles, and melts at 88—89°; with hydrobromic acid, it yields *dibromovaleric acid*,  $C_5H_8Br_2O_2$ , which crystallises in large, lustrous, colourless, apparently rhombic, prisms, melts at 51—52°, and is not identical with either of the three hitherto known dibromovaleric acids.

C. F. B.

**Combination of Aluminium Chloride with Nitro-derivatives of the Benzene Series.** By G. PERRIER (*Compt. rend.*, 1895, 120, 930—932).—The compound,  $Al_2Cl_6 \cdot 2PhNO_2$ , described by Stockhausen and Gattermann (*Abstr.*, 1893, i, 161), is readily obtained by the interaction of the calculated proportions of its proximate constituents in presence of carbon bisulphide, and forms large, crystalline lamellæ, melting at 85—87°. Other nitro-derivatives under like conditions yield strictly analogous compounds, as follows. *Paranitrotoluene*, large, yellow lamellæ, melting at 105°; *α-nitronaphthalene*, red needles, melting at 115° to a brown liquid, which decomposes suddenly at 130°; *metadinitrobenzene*, small, yellowish scales, melting at 65—67°; *dinitrotoluene*, a yellowish, oily liquid, which solidifies to an amorphous mass on cooling; *paranitranisole*, small, yellow crystals, melting at 120° to an orange liquid, with a violet fluorescence; *orthonitranisole*, a liquid, formed with difficulty, owing to the decomposition of a large proportion of the ether by the aluminium chloride.

According to Stockhausen and Gattermann (*loc. cit.*), acetic chloride combines with orthonitranisole and orthonitrophenetole in presence of aluminium chloride. Experiments with acetic and benzoic chlorides

and various nitro-derivatives of the hydrocarbons alone, or in the presence of carbon bisulphide, show, however, that this reaction is not applicable to nitro-derivatives of hydrocarbons. The acid chlorides have no action on the compounds of the nitrohydrocarbons with aluminium chlorides. If aluminium chloride is added gradually to a mixture of the nitro-hydrocarbon and the acid chloride, the compound of the nitrohydrocarbon with aluminium chloride is the sole product. If the nitrohydrocarbon is added to the double compound of aluminium chloride and the acid chloride, the latter is displaced, and the compound of the nitrohydrocarbon and aluminium chloride is formed.

C. H. B.

### Action of Phosphorus Pentachloride on Aromatic Ethers.

By WILHELM AUTENRIETH (*Arch. Pharm.*, 1895, 233, 26—42).—The author has investigated the action of phosphorus pentachloride on mixed ethers of the benzene, naphthalene, and quinoxaline series, and finds that in all cases it reacts as a chlorinating agent, yielding a monochlorinated ether, together with phosphorus trichloride and hydrogen chloride. If the ether and pentachloride are mixed together and heated to 30°, a vigorous action takes place, the mass melts to a dark red liquid, hydrogen chloride is evolved, and phosphorus trichloride passes over between 70° and 90°. In no case, even with a large excess of the pentachloride and at a high temperature, was the formation of phosphorus oxychloride and the decomposition of the ether, as in the case of aliphatic ethers (Bachmann, *Abstr.*, 1883, 726) observed.

*Parachloranisoil*, obtained by the action of phosphorus pentachloride on anisoil, is a colourless, aromatic oil, which boils at 195—196°, whereas Beilstein and Kurbatow (*Annalen*, 176, 30) give 198—202° as the boiling point. On hydrolysis with concentrated hydrochloric acid at 200°, it yielded the parachlorophenol, which was characterised by the formation of its benzoyl derivative; the latter crystallises in pearly plates, which melt at 86°.

*Parachlorophenetol* is a thick, colourless oil, with an intense aromatic odour. It is slightly volatile with steam, and boils at 212—215°.

*α-Chloro-β-naphthyl methyl ether*, (Cl : OMe = 1 : 2) was prepared from β-naphthyl methyl ether and phosphorus pentachloride; it forms white, pearly plates, and melts at 78°. It is insoluble in water, but readily soluble in most organic solvents. The α-chloro-β-naphthol, obtained by the hydrolysis of the ether with concentrated hydrochloric acid at 200—250°, forms colourless, glistening plates and needles, which melt at 70°. It sublimes on further heating, and gives with alkalis violet fluorescent solutions. Its benzoyl derivative crystallises in plates, and melts at 101°.

*Ethoxytrichloroquinoxaline* is obtained by the action of phosphorus pentachloride (3 mols.) on the ethoxydihydroxyquinoxaline (1 mol.) of Autenreith and Hinsberg (*Abstr.*, 1892, 734). It crystallises in small, yellowish, glistening needles, and melts at 144°. It is insoluble in water, but soluble in alcohol, ether, and chloroform. *Hydroxytrichloroquinoxaline* is obtained when this ether is hydrolysed with concentrated hydrochloric acid at about 200°. This hydroxytrichloroquinoxaline is practically insoluble in water, alcohol, ether, chloroform,

and acetic acid. It is, however, soluble in alkalis and in concentrated acids.

For the purposes of identification, the benzoyl derivatives of para and orthochlorophenol were prepared and examined. The para-compound melts at  $86^{\circ}$  (see above), whereas the ortho-derivative is a highly refractive liquid, which boils at  $314\text{--}316^{\circ}$ .

When parachlorophenol is treated with benzene sulphochloride according to the Baumann-Schotten-Hinsberg method (Abstr., 1891, 49), the *parachlorophenylic benzenesulphonate*,  $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\text{Ph}$ , is formed. This is a colourless, odourless oil, which is insoluble in water, but miscible with alcohol and with ether. J. J. S.

### Tolyl Derivatives of Sulphur, Selenium, and Tellurium.

By F. ZEISER (*Ber.*, 1895, 28, 1670—1675).—Krafft and Lyons have already shown that the mercury in mercury diphenyl may be readily displaced by the elements of the sulphur group (Abstr., 1894, i, 448); in the present paper, the author shows that the mercury ditolyls behave in a similar manner towards those elements. *Diorthotolyl telluride*,  $(\text{C}_6\text{H}_4\text{Me})_2\text{Te}$ , is prepared by heating mercury diorthotolyl with tellurium in a sealed tube at  $225\text{--}235^{\circ}$ ; it crystallises from alcohol in small, rectangular plates, melts at  $37\text{--}38^{\circ}$ , and boils at  $202.5^{\circ}$  under 16 mm. pressure. It combines with bromine yielding the *tellurobromide*,  $(\text{C}_6\text{H}_4\text{Me})_2\text{TeBr}_2$ , which forms pale yellow prisms with oblique terminal surfaces, and melts at  $182^{\circ}$ . The corresponding *diparatolyl telluride* forms small, lustrous, flat, white prisms, melts at  $63\text{--}64^{\circ}$ , and boils at  $210^{\circ}$  under 16 mm. pressure. The *tellurobromide* crystallises in thin, lustrous, yellow, rhombic tablets, melting at  $201^{\circ}$ .

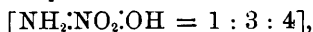
*Diorthotolyl selenide*,  $(\text{C}_6\text{H}_4\text{Me})_2\text{Se}$ , obtained by heating mercury diorthotolyl with selenium, crystallises from alcohol in small, rectangular plates, melting at  $61\text{--}62^{\circ}$ , and boiling at  $186^{\circ}$  under 16 mm. pressure. The *selenobromide* is obtained as a brownish-red precipitate of small needles; it is very unstable, decomposing at  $84^{\circ}$ . If the selenide is oxidised with nitric acid of sp. gr. 1.4, it yields a solution of the *nitrate* of diorthotolylselenyl oxide, which, on treatment with concentrated hydrochloric acid, gives a crystalline precipitate of *diorthotolyl selenochloride*,  $(\text{C}_6\text{H}_4\text{Me})_2\text{SeCl}_2$ , the latter melts at  $152\text{--}153^{\circ}$  with decomposition, and on careful treatment with soda is converted into *diorthotolyl selenic oxide*,  $(\text{C}_6\text{H}_4\text{Me})_2\text{SeO}$ , which forms glassy plates, and melts at  $116^{\circ}$ ; it dissolves in hydrochloric acid, regenerating the chloride.

*Diparatolyl selenide* forms colourless, prismatic crystals, melting at  $69\text{--}69.5^{\circ}$ , and boiling at  $196\text{--}196.5^{\circ}$  under 16 mm. pressure, and the *selenobromide* crystallises in microscopic, yellow prisms with oblique terminal surfaces, and melts and decomposes at  $162^{\circ}$ . The *selenochloride* is a white precipitate, and melts at  $177\text{--}178^{\circ}$ , and the *selenic oxide* crystallises in small, white needles; it melts at about  $90^{\circ}$ , turns red litmus blue, and, like the ortho-compound, combines with acids.

*Diorthotolyl sulphide* is obtained by heating mercury diorthotolyl with sulphur, and crystallises in lustrous, colourless, rectangular plates, melting at  $64^{\circ}$ , and boiling at  $175^{\circ}$  under 16 mm. pressure.

H. G. C.

**Nitroquinones.** By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1386—1388).—The author, in conjunction with Zeitlin, has previously shown (*Abstr.*, 1894, i, 184) that substituted diazobenzeneimides, when heated with sulphuric acid, lose nitrogen, and yield substituted amidophenols, probably with the formation of phenylhydroxylamine derivatives as intermediate products. When metanitrodiazobenzene-imide is treated with sulphuric acid, the nitroamidophenol,



is formed. When this is oxidised with potassium permanganate, the nitroquinone,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{O}_2$ , is obtained. If the oxidation is carried out with small quantities of the phenol (0.5—1.0 gr.), the resulting quinone is quite pure. It is insoluble in cold water, and only slightly soluble in hot; dissolves sparingly in ether, benzene, and light petroleum, more readily in alcohol, acetic acid, acetone, and chloroform. The alcoholic solution, when rapidly cooled, yields golden-yellow crystals, which decompose at  $206^\circ$ . It is not volatile with steam, but dissolves in alkalis to a brownish-violet solution. When warmed with aniline and alcohol, it forms a *dianilidonitroquinone*,  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_4$ , which crystallises from alcohol or acetic acid in small needles of melting point  $260^\circ$ . In spite of many attempts, the author has not succeeded in preparing Étard's nitroquinone by the action of chromyl chloride on nitrobenzene. J. J. S.

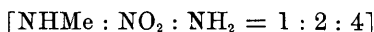
**Constitution of Phenoquinone.** By C. LORING JACKSON and GEORGE OENSLAGER (*Ber.*, 1895, **28**, 1614—1617; compare *Abstr.*, 1893, i, 563).—It is suggested that phenoquinone has a constitution similar to that of a hemiacetal, and the formula  $\text{C}_6\text{H}_4(\text{OH})_2(\text{OPh})_2$  is proposed. It is shown that this formula is in harmony with the chemical behaviour of the substance. It would lead us to anticipate the existence of salts of phenoquinone, and these have been said not to exist. The authors have, however, prepared a blue *disodium salt* by treating phenoquinone with an alkaline solution of sodium  $\beta$ -naphthoxide, and also by the direct addition of sodium phenoxide to quinone in ethereal solution. C. F. B.

**Guaiacol and its Derivatives.** By FRITZ LÜDY (*Chem. Centr.*, 1895, i, 32; from *Schweiz. Woch. Pharm.*, 1895, **32**, 469—473).—A method for preparing pure crystalline guaiacol is given; it melts at  $28.5^\circ$ , boils at  $203\text{—}204^\circ$ , has a density of 1.1355—1.1370 at  $18^\circ$ , and is soluble in 50 parts of water. A modification of Reimer's method of synthesising oxyaldehydes is given, and serves in a patented process for preparing vanillin. W. J. P.

**Nitrotoluquinol.** By FRIEDRICH KEHRMANN and M. TIKHVINSKY (*Ber.*, 1895, **28**, 1542—1543).—Acetyldinitrotoluquinol (*Abstr.*, 1889, 969) is accompanied by a small amount of *acetylnitrotoluquinol*. This crystallises in long, lustrous, lemon-yellow needles melting at  $118\text{—}120^\circ$ . *Nitrotoluquinol* crystallises in yellowish-red needles, and melts at  $122\text{—}124^\circ$ . It forms a deep bluish-violet coloured solution in alkalis. The *diacetyl-compound* crystallises in colourless tablets melting at  $101\text{—}104^\circ$ . A. H.

**Action of Alcoholic Ammonium Sulphide on 1:2:4-Amido-dinitrobenzene.** By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 1707—1709).—Dinitraniline [ $\text{NH}_2 = 1$ ;  $(\text{NO}_2)_2 = 2:4$ ], when reduced with alcoholic ammonium sulphide, yields two nitrophenylenediamines, the orthodiamine is deposited first; the mother liquid is then evaporated to dryness, the residue extracted with dilute hydrochloric acid, and the remaining ortho-compound precipitated with dilute ammonia; if the filtrate is mixed with concentrated ammonia, and allowed to cool, the paradiamine is deposited. It is identical with Ladenburg's compound from nitrodiacetoparaphenylenediamine.

Dinitromethylaniline behaves like dinitraniline, and the amines are separated in a similar manner, the *para*-compound



crystallises from water in almost black plates with a bronze lustre; it melts at  $109\text{--}110^\circ$ , and is red when powdered. The *salts* crystallise readily, and their solutions, like that of the base, resemble magenta in colour.

1:2:4-Dinitrodiphenylamine, when reduced with ammonium sulphide, yields, in addition to the orthophenylenediamine, a second base which appears to be the *para*-compound. Heim's conclusion, that the reduction of aromatic dinitramines by means of ammonium sulphide gives orthodiamines only, is therefore incorrect.

J. B. T.

**Nitro- and Amido-derivatives of Paraditolylamine.** By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 1647—1650).—In his work on the constitution of the safranines (this vol., i, 219), the author mentioned that a new safranine may be obtained by the action of quinone dichlorimide on metamidoditolylamine; in the present paper, he gives a detailed description of the mode of preparation and properties of the latter. In order to prepare it, paraditolylamine is nitrated in sulphuric acid solution at  $-10^\circ$ , and the resulting crude metanitroditolylamine, which contains large quantities of unaltered ditolylamine, is reduced by zinc-dust in acetic acid solution; the product is then made alkaline, extracted with ether, and the evaporated extract distilled in a current of coal gas or carbonic anhydride. The distillate consists of a mixture of the amido-derivative and ditolylamine, which may be separated by fractional crystallisation from light petroleum. *Metamidoditolylamine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , which crystallises in well-developed, colourless prisms, melting at  $71^\circ$  (corr.), may be readily diazotised.

If paraditolylamine is nitrated in acetic acid solution, it yields a *tri-nitroparadiphenylamine*,  $\text{C}_{14}\text{H}_{12}\text{N}(\text{NO}_2)_3$ , which crystallises from chloroform in prisms melting at  $268^\circ$ .

H. G. C.

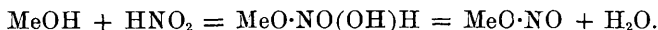
**Maximum Temperature of Formation and Temperature of Decomposition of some Aromatic Diazochlorides.** By G. ODDO (*Gazzetta*, 1895, **25**, i, 327—339).—The substances obtained by the author during his attempts to prepare the fluoronitrobenzenes (*Abstr.*, 1891, 553) are not amidazo-compounds, as he supposed at the time, but diazoamido-derivatives; the compounds described as the meta-



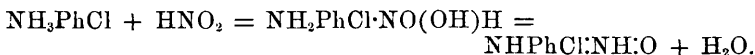
and para-dinitramidoazobenzenes are the meta- and para-dinitrodi-azoamidobenzenes described by Meldola and Streatfeild (*Trans.*, 1887, 102, 434), and behave as such on heating with hydrochloric acid, fusion with  $\beta$ -naphthol, or treatment with ethylic iodide and alcohol. In order to explain the formation of these compounds, it must be admitted that in the process employed (*loc. cit.*) the diazofluoride is first formed and subsequently condenses with a second molecule of the base at a high temperature. The author has made a series of experiments, demonstrating that diazo-salts can be formed at 90–100°; thus, on passing nitrous anhydride into a hydrochloric acid solution of paranitraniline at 85–90°, paranitrodiazobenzene is formed, and is even produced at 100°, although the dry salt explodes at 85°. Further, dry metanitrodiazobenzene chloride explodes at 118°, and dry  $\alpha$ -diazonaphthalene and orthodiazophenol chlorides decompose without explosion at 96° and 152° respectively, whilst the same salts can be prepared at 100°, 60°, and below 60° respectively by the ordinary method of diazotising by aid of amyl nitrite.

W. J. P.

**Constitution of Diazo-compounds.** By R. WALTHER (*J. pr. Chem.*, 1895, [2], 51, 528–531 and 581–584).—It is generally acknowledged that the formula for diazobenzene which is at present accepted fails to explain all the reactions of the compound. Particularly is this the case with the reaction between diazobenzene chloride and bromaniline on the one hand, and that between diazobromobenzene chloride and aniline on the other hand; for these two reactions yield the same compound, whereas, according to Kekulé's formula for diazobenzene, they should yield isomerides. If nitrous acid be supposed to contain pentavalent nitrogen, the formation of an alkylic nitrite from an alcohol and nitrous acid could be expressed thus—



So also the reaction between nitrous acid and aniline hydrochloride would be—



The latter formula would represent diazobenzene chloride in aqueous solution, and the constitution of free diazobenzene would be represented by  $\text{PhN} \cdot \text{NH} \cdot \text{O}$ . The compound produced by the interaction of diazobenzene and aniline would then have the formula



which would account for the identity of the products in the reactions referred to above.

Meldola and Streatfeild have shown that the reaction between metanitrodiazobenzene and paranitraniline, on the one hand, and that between paranitrodiazobenzene and metanitraniline on the other hand, yield one and the same compound. The constitution of this may be either  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$  or  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .

3

1

1

4

3

1

1

4

If the first of these be correct, the decomposition of the compound with hydrochloric acid should yield metanitrochlorobenzene and paranitraniline, whilst the second formula should yield paranitrochlorobenzene and metanitraniline. As a fact, all four products are obtained when the compound is decomposed by hydrochloric acid.

If the constitution of diazobenzene derivatives be that suggested by the author, the above anomaly, and several similar ones which the author quotes in the paper, disappear. For in this case the product of the interactions just discussed would be represented by the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}^1\text{NH}\cdot\text{N}^1\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , and a compound of this structure may be expected to be hydrolysed into 1 : 3- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}^1\text{NH}\cdot\text{O}$  and 1 : 4- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , equally as well as into 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}^1\text{NH}\cdot\text{O}$  and 1 : 3- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . The diazobenzene would immediately yield chloronitrobenzene with the hydrochloric acid, so that all four products named above may be expected.

A. G. B.

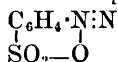
**Diazohaloid Compounds.** By EUGEN BAMBERGER (*J. pr. Chem.*, 1895, [2], 51, 585—591). This is a reply to Hantzsch (this vol., i, 349). Whilst it is true that a few diazohalogen compounds, particularly such as contain two or more halogen atoms, are unstable in the solid state but stable in solution, it is not permissible to generalise from these cases. Other points in Hantzsch's paper are criticised, and the author concludes that the feeble acid properties of diazobenzene are no argument against the ammonium formula  $\text{N}^+\text{NPh}\cdot\text{OH}$ , since it is by no means uncommon for nitrogen which replaces three hydrogen atoms to impart acidity (compare  $\text{N}^+\text{CH}$  from  $\text{CH}_4$ ;  $\text{N}^+\text{C}\cdot\text{OH}$  from  $\text{CH}_3\cdot\text{OH}$ ).

A. G. B.

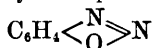
**Diazonium Compounds and Normal Diazo-compounds.** By ARTHUR HANTZSCH (*Ber.*, 1895, 28, 1734—1753).—Since the discovery of the isodiazo-compounds, all the diazo-compounds previously known have been described as normal compounds, in contradistinction to the later known "iso"-compounds. Recently Bamberger has adopted Blomstrand's formula,  $\text{N}^+\text{N}\cdot\text{R}\cdot\text{OH}$ , for the "normal" compounds, retaining the azo-formula,  $\text{RN}\cdot\text{N}\cdot\text{OH}$ , for the iso-diazo-compounds. From the results of his investigations, the author has concluded that diazo-compounds of both types do in reality exist, but that some of the so-called normal diazo-derivatives are of one type and some of the other, and sums up his conclusions as follows. (1) The salts of diazobenzene with oxy-acids, and also the haloid salts, contain the radicle  $\text{N}^+\text{NPh}$ , which is strictly analogous to ammonium, behaving in all respects as a compound alkali-metal, and may therefore be termed "diazonium." The metallic salts, sulphonic acids, and cyanides have a composition analogous to that of the azo-compounds and oximes, containing the true diazo-radicle,  $\text{Ph}\cdot\text{N}\cdot\text{N}$ , and these are capable of existing in two stereometric modifications, as already shown by the author. (2) Diazonium salts are converted very readily, especially in alkaline solution (that is, by means of hydroxyl ions), into normal syn-diazo-compounds, the reverse change being brought about by

acid. (3) The typical diazo-decomposition,  $\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{R} = \text{PhR} + \text{N}_2$ , only takes place directly with the syn-diazo-compounds, the other isomerides first undergoing an intramolecular change with formation of the isomeric syn-derivative. (4) Inner anhydrides of both diazonium compounds and of syn-diazo-compounds can exist, the former being analogous to betaine, and the latter to azimidobenzene.

Benzenediazoniumsulphanic acid.



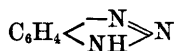
Syn-diazophenol.



Betaine.



Azimidobenzene.



(5) No diazo-haloids of the formula  $\text{RN}\cdot\text{NCl}$  are at present known, but coloured labile double compounds with cuprous haloids have been prepared, which are totally different from the double salts of the diazonium compounds, the latter being colourless, stable, and very similar to the corresponding ammonium and potassium double salts.

In support of statement (1), the author adduces the neutrality of the solutions and the fact that the electrolytic dissociation of the solutions of these salts corresponds very closely with that of the analogous potassium and ammonium salts under similar conditions. (The detailed experiments on this point will be published later.) In further agreement with the alkaline character of the diazonium radicle is the formation of soluble salts even with the weakest acids; thus *diazonium carbonates* may be prepared by the action of freshly precipitated silver carbonate on solutions of the chloride, and the *nitrites* and *acetates* may be obtained in a similar manner. The solutions of benzenediazonium, and paranitrobenzenediazonium carbonate are unstable, but that of parabromobenzenediazonium carbonate is fairly stable at  $0^\circ$ ; they have an alkaline reaction, and on boiling, decompose with evolution of nitrogen, but the tarry products contain scarcely any phenol. The solution of parabromobenzenediazonium nitrite is also the most stable, and on boiling yields nitrogen, but scarcely any phenol or bromonitrobenzene; none of the salts could be obtained in the solid form. The formation of stable double salts still further confirms the analogy of the diazonium and ammonium compounds; in addition to the already known platinochlorides, the author has prepared *cobaltinitrites*, which form yellow microcrystalline powders, but cannot readily be obtained pure. Of more importance are the double salts with mercuric chloride, obtained by the addition of mercuric chloride solution to aqueous diazonium haloids; *benzenediazonium mercuriochloride*,  $\text{PhN}_2\cdot\text{HgCl}_3$ , forms slender, white needles, decomposing at  $122^\circ$ , and closely resembles ammonium mercuriochloride,  $\text{NH}_4\text{HgCl}_3$ , and, like the latter, crystallises either in the anhydrous form or with 1 mol.  $\text{H}_2\text{O}$ . *Parachlorobenzenediazonium mercuriochloride*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}\cdot 2\text{HgCl}_2 + 2\text{H}_2\text{O}$ , is so stable that it may be recrystallised from boiling water, and then melts with decomposition at  $139\text{--}140^\circ$ ; it corresponds with the potassium mercuriochloride,  $\text{KCl}\cdot\text{HgCl}_2 + 2\text{H}_2\text{O}$ . A double salt of diazonium chloride and

mercuric cyanide,  $C_6H_5 \cdot N_2Cl \cdot 2Hg(CN)_2 + H_2O$ , can be prepared in a similar manner, and crystallises in needles which explode at  $107^\circ$ .

The proofs that the diazobenzene metallic salts, sulphonic acids, and cyanides have the azo-formula are mainly of an indirect nature, depending chiefly on the great differences observed between their properties and those of the diazonium compounds. If the potassium and silver salts had the constitution  $N:NPh \cdot OK$  (or  $OAg$ ), diazonium hydroxide must possess simultaneously basic and acid properties, a combination which has, however, never been observed in the case of the alkali-metals or compound radicles forming hydroxides analogous to those of the alkali-metals. In the case of the sulphonic acids, if these had the diazonium constitution it would form the first instance of the presence of the group  $N \cdot SO_3M$  in a derivative of an ammonium base, and moreover, such compounds should, if the metal yields colourless salts, be also colourless, whereas the diazosulphonates are all coloured, like the azo-compounds. For the diazocyanides, in addition to the grounds already mentioned against the diazonium constitution, the author adduces the facts that although the diazonium haloids are analogous in almost all respects to the corresponding alkali salts, the cyanides differ totally from the alkali cyanides, as they are coloured, are insoluble in water, do not conduct electricity, and appear to be incapable of forming double salts. The isomerism of these two salts cannot therefore be explained by supposing that the one is a diazonium and the other a diazo-derivative, but these facts are all in agreement with the supposition that they are stereometric isomerides, each being a true diazo-derivative. That the two diazosulphanilic acids are both true diazo-compounds has been shown by Gerilowski, whose results will shortly be published, and in this case also the only tenable hypothesis is that they are stereo-isomerides.

The second of the author's conclusions, namely, that the diazonium compounds are readily converted into syn-diazo-compounds, follows from the fact already mentioned, that benzenediazonium chloride is readily converted into the syn-diazobenzene potassium and the sulpho-nate and cyanide. A direct proof is also found in the fact that when the so-called diazosulphanilic acid (which, as will be shown in a later paper, is in reality the inner anhydride of benzenediazoniumsulphonic acid, and is a neutral substance) is treated with alkali (1 mol.), it is slowly converted into a syn-diazobenzenesulphonate, the solution again becoming neutral. Had the salt formed been a diazonium salt of the formula  $\begin{matrix} C_6H_4 \\ SO_3 \end{matrix} > N:N$ , it would certainly have had a strongly

alkaline reaction. The conversion of diazonium into diazo-compounds is brought about most readily in alkaline solution, that is, under the influence of hydroxyl ions. The change from the diazonium to the diazo-constitution also explains the action of silver oxide on the diazonium haloids, which is otherwise not readily understood. The action does not proceed according to the equation  $PhN_2Cl + AgOH = AgCl + PhN_2 \cdot OH$ , but requires double the amount of silver oxide, silver chloride and diazobenzene silver being formed,  $PhN_2Cl + Ag_2O = PhN_2 \cdot OAg + AgCl$ . The alkaline nature of moist silver

oxide is sufficient to bring about the conversion of the diazonium radicle into the diazo-radicle, and simultaneously with its formation the resulting diazo-hydroxide is converted into the silver compound. These experiments were repeated with numerous other diazonium haloids, among which the bromides were found the most suitable; these may be readily prepared from the corresponding amido-compound by diazotising in alcoholic solution with hydrobromic acid and amyl nitrite, and precipitating with ether; *parabromobenzenediazonium bromide*,  $\text{BrC}_6\text{H}_4\text{N}_2\text{Br}$ , crystallises from hot alcohol in large yellowish plates, *paranitrobenzenediazonium bromide*,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{Br}$ , in lemon-yellow, very explosive plates. and *ortho-chlorobenzenediazonium bromide*,  $\text{ClC}_6\text{H}_4\text{N}_2\text{Br}$ , in straw-yellow needles, the aqueous solution of which hardly evolves any nitrogen on boiling.

When diazonium sulphates and carbonates are treated with baryta water, they also are not simply converted into barium sulphate or carbonate and the diazonium hydroxide, but yield in addition considerable quantities of syn-diazobenzene barium. The hydroxide formed consists chiefly if not exclusively of the syn-diazohydroxide.

The third conclusion, that only the syn-diazo-compounds undergo the typical diazo-reaction with evolution of nitrogen, is borne out by the behaviour of the syn-diazosulphonates and of syn-diazobenzene cyanide described in previous papers by the author. A new proof is found in the behaviour of free diazosulphanilic acid, which, as will be shown in a future paper by Gerilowski, is a diazonium compound, and is perfectly stable in solution at the ordinary temperature, whilst the corresponding syn-diazo-salt, which may be readily obtained from it, loses the whole of its nitrogen under similar circumstances. Further, if the diazonium compounds underwent direct decomposition into nitrogen and benzene in a manner analogous to the decomposition of ammonium chloride into ammonia and hydrochloric acid, the action should proceed more readily as the anion becomes less negative; but it is found that, on the contrary, the diazonium carbonate undergoes the typical decomposition much less readily than the chloride, and the latter yields phenol and not chlorobenzene. This is readily explained if we assume that water, like the alkalis, first converts the diazonium compound into syn-diazohydroxide and free acid; the former then decomposes into phenol and nitrogen, the action proceeding the more readily as the acid liberated is more active.

The reasons for the fourth conclusion will be considered in a later paper. The facts on which the fifth conclusion is based have already been partly given above, where it has been shown that colourless diazonium double salts with mercuric salts can be prepared. True diazo-haloids have not yet been prepared, but the author has succeeded in obtaining double salts which differ totally from those of the diazonium derivatives. These are formed with cuprous chloride and bromide, the latter salts being the most stable. They are obtained by dissolving the cuprous salt in hydrochloric acid and adding a solution of the pure diazonium chloride. *Syn-diazobenzene*

*cuprobromide*,  $\text{Ph}\cdot\text{N}\overset{\text{H}}{\underset{\text{BrN}}{\parallel}},\text{Cu}_2\text{Br}_2$ , forms large, reddish-yellow needles, and

decomposes on addition of water into cuprous bromide, nitrogen,

and bromobenzene, no diazonium bromide being re-formed. *Para-bromosyndiazobenzene cuprobromide*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{N} \begin{smallmatrix} \text{N} \\ \text{Br} \end{smallmatrix} \text{Cu}_2\text{Br}_2$ , is similar to the foregoing, but is of a darker red. They differ from the diazonium salts, inasmuch as they are strongly coloured, although cuprous salts are themselves colourless, and also in their stability and in the manner in which they undergo decomposition. H. G. C.

**Azo- and Azimido-Compounds.** By WILLIAM G. MIXTER (*Amer. Chem. J.*, 1895, **17**, 449—453).—*Benzoylmetazoparatoluidide*,  $[\text{Me} : \text{NHBz} : \text{N}_2 = 1 : 4 : 5]$ , is prepared by reducing benzoylmetanitroparatoluidide in alcohol with zinc and ammonia, and crystallising the precipitate from glacial acetic acid. It forms orange coloured crystals, melts at  $242^\circ$ , and is nearly insoluble in alcohol.

*Acetylmetazo-orthotoluidide*,  $[\text{Me} : \text{NHAc} : \text{N}_2 = 1 : 2 : 5]$ , from acetylmetanitro-orthotoluidide (m. p.  $202^\circ$ ; Beilstein and Kuhlberg, give  $197^\circ$ ), crystallises in orange "fibres," does not melt at  $310^\circ$ , and is not very soluble in hot glacial acetic acid.

*Benzoylazo-xylidide*,  $[\text{Me}_2 : \text{NHBz} : \text{N}_2 = 1 : 3 : 4 : 5]$ , from benzoylnitro-xylidide (m. p.  $187^\circ$ ) separates from hot glacial acetic acid in orange "fibres," and decomposes without melting at  $280$ — $290^\circ$ .

*Benzoylazimidotoluene*,  $[\text{Me} : \text{N}_2 : \text{NBz} = 1 : 4 : 5]$ , is prepared by dissolving benzoyltoluylenediamine in hydrochloric acid, and passing nitrous fumes through the solution; the new compound is at once precipitated. It crystallises from alcohol in white "fibres," and melts at  $125^\circ$ .

*Azimido-xylene* was prepared by treating benzoylazimido-xylene (m. p.  $111^\circ$ ) with hot concentrated hydrochloric acid and adding water; on cooling, benzoic acid crystallises and the azimido-xylene may be precipitated from the solution as a white powder by the addition of ammonia. It melts at about  $186^\circ$  and dissolves in hot water, alcohol, ether, nitric acid, and hydrochloric acid. A silver compound was prepared. A. G. B.

**Action of Alcohols on Metadiazobenzenesulphonic Acid.** By W. B. SHORER and H. E. KIEFER (*Amer. Chem. J.*, 1895, **17**, 454—461).—In a series of experiments parallel with that conducted with paradiazobenzenesulphonic acid (*Abstr.*, 1893, i, 639), the following conclusions have been arrived at:—(1) Methylic alcohol when heated with metadiazobenzenesulphonic acid under various pressures gives both benzenesulphonic acid and methoxybenzenesulphonic acid. At the highest pressures, the methoxy-compound is formed in greatest excess. (2) Ethylic alcohol gives similar results. (3) Propylic alcohol at ordinary pressures gives both reactions.

The metadiazocompound is decomposed with much greater ease than is the para-compound, a few minutes generally sufficing in place of from two to eight hours. A. G. B.

**Conversion of Hydrazines into Paradiamines.** By JOHANNES THIELE and L. H. WHEELER (*Ber.*, 1895, **28**, 1538—1539).—Hydrazines, in which there is no substitution in the para-position, are

converted into paradiamines when heated with fuming hydrochloric acid (1—3 parts) at 200°; dilute sulphuric acid is not suitable, the yield being smaller, and part of the hydrazine being oxidised. Paraphenylenediamine and methylparaphenylenediamine were obtained in this manner from phenylhydrazine and unsymmetrical methylphenylhydrazine respectively. Paratolyldiazine, and  $\beta$ -naphthylhydrazine gave paratoluidine, and  $\beta$ -naphthylamine respectively, together with ammonium chloride. Unsymmetrical diphenylhydrazine yielded only resinous products.

J. B. T.

**Action of Phenylhydrazine on Chloracetanilide.** By HANS RUPE and GEORG HERBERLEIN (*Ber.*, 1895, 28, 1717—1719).—The chief product of the interaction of phenylhydrazine and chloracetanilide is the unsymmetrical hydrazine derivative,



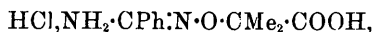
which crystallises in colourless needles and melts at 149°. A second compound, probably phenylhydrazineglyoxalic anilide, is formed simultaneously, it melts at 135°, and is more readily soluble in ether. Phenylhydrazidacetanilide readily reacts with ketones and aldehydes; the compounds with formaldehyde, benzaldehyde, and ethylic acetoacetate melting at 220°, 223°, and 158° respectively. The nitroso-derivative melts at 144° and is identical with the nitrosamine from anilidoacetanilide. When heated with sodium ethoxide, the hydrazidanilide yields a compound which is insoluble in acids and alkalis and melts at 273°; dilute alkalis or acids convert the hydrazidanilide into a substance which melts at 205°, and dissolves readily in alkalis. The aniline derivatives of chloracetic acid and those of ethylic chloracetate, yield compounds with phenylhydrazine which are quite different from one another.

J. B. T.

**Hydroxylamineisobutyric acid.** By ALFRED WERNER and F. BIAL (*Ber.*, 28, 1895, 1374—1379).—By the action of benzenylamidoxime (1 mol.) on ethylic  $\alpha$ -bromisobutyrate (1 mol.) and potassium hydroxide (2 mols.) in alcoholic solution, the authors have obtained three different products, namely the potassium salt, esonhydride and ethylic salt of benzenylamidoximeisobutyric acid. The alcohol was got rid of by evaporation and the potassium salt and the anhydride removed by extracting the residue with dilute soda. On treating the insoluble oily residue with dilute hydrochloric acid, a small quantity of dibenzenylazoxime,  $\text{CPh}\langle\begin{smallmatrix} \text{N} \\ \text{N}\cdot\text{O} \end{smallmatrix}\rangle\text{CPh}$ , remained behind, but the amidoethereal salt dissolved in the form of its hydrochloride. This forms large crystals which melt at 154—155°. It is soluble in alcohol but insoluble in benzene and light petroleum. From this hydrochloride, ethylic  $\alpha$ -benzenylamidoximeisobutyrate,  $\text{NH}_2\cdot\text{CPh}\cdot\text{NO}\cdot\text{CMe}_2\cdot\text{COOEt}$ , was obtained on warming with potash; it melts at 37—38°, is readily soluble in ether and benzene, less soluble in alcohol and apparently insoluble in light petroleum.

*Benzenylamidoximeisobutyric esonhydride*,  $\text{NH}\langle\begin{smallmatrix} \text{CO}\cdot\text{CMe}_2 \\ \text{CPh}=\text{N} \end{smallmatrix}\rangle\text{O}$ , is the main product formed, it can be isolated by acidifying the alka-

line solution above mentioned with dilute hydrochloric acid. It forms large plates, melts at  $112^{\circ}$ , and is insoluble in water and light petroleum, but dissolves in alcohol, ether, and benzene. It also dissolves readily in alkalis, and when heated with concentrated hydrochloric acid yields the *hydrochloride of the amido-acid*,



which crystallises from water in colourless prisms and melts at  $182\text{--}185^{\circ}$ . *Benzenylamidoximeisobutyric acid* is best obtained by the hydrolysis of the ethylic salt described above. It crystallises from alcohol in fan shaped needles which melt at  $112^{\circ}$ . The acid is readily soluble in alcohol and ether, sparingly in benzene, and insoluble in light petroleum.

*$\alpha$ -Benzenylchloroximeisobutyric acid*,  $\text{CPhCl} \cdot \text{N} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{COOH}$ , is obtained by the action of sodium nitrite solution at the ordinary temperature on a solution of the amido-acid in hydrochloric acid. It crystallises in plates, and is readily soluble in glacial acetic acid, alcohol, and ether, but only sparingly in hot water, and melts at  $81^{\circ}$ . The corresponding *bromo-acid* melts at  $80^{\circ}$ . If either the chloro- or bromo-acid is treated with sodium ethoxide *ethylbenzoximeisobutyric acid*,  $\text{OEt} \cdot \text{CPh} \cdot \text{N} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{COOH}$ , is formed; this is an oily substance which is insoluble in water, but dissolves readily in alcohol or ether. When heated with hydrochloric acid (50 per cent.), it is hydrolysed into ethylic benzoate and  *$\alpha$ -hydroxylamineisobutyric acid hydrochloride*. The former may be removed by extraction with ether, and on evaporating the aqueous solution the hydrochloride separates in the form of prisms, which melt at  $160\text{--}162^{\circ}$ .

*$\alpha$ -Hydroxylamineisobutyric acid*,  $\text{NH}_2 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{COOH}$ , may be obtained by the action of freshly precipitated silver oxide (about 2 mols.) on the hydrochloride (1 mol.) and subsequent removal of the silver with hydrogen sulphide. The acid crystallises from water in crusts, melts at  $137^{\circ}$  and is readily soluble in water and in alcohol, but insoluble in ether, benzene, and light petroleum. The *nitrate* is readily soluble in water, and melts at  $140^{\circ}$ . The *sulphate* is more sparingly soluble in water than the nitrate, and melts at  $185\text{--}188^{\circ}$ .  
J. J. S.

**Action of Benzimidomethyl Ether on Aromatic Ortho-compounds.** By H. L. WHEELER (*Amer. Chem. J.*, 1895, 17, 397—403).—*Benzimidomethyl ether*, was prepared by treating silver benzamide, suspended in dry ether, with excess of methylic iodide, adding more ether after the lapse of several days, filtering, and evaporating the ether (compare Tafel and Enoch, *Abstr.*, 1890, 491). It is a pale yellow oil, still liquid at  $-30^{\circ}$ , and soluble in acids, but precipitable from such solutions by alkalis. The *platinochloride* was prepared.

Benzimidomethyl ether undergoes condensation with orthamidoaromatic compounds when heated with them, methylic alcohol and ammonia being eliminated. In this way there have been prepared benzenylorthamidophenol (this *Journal*, 1877, i, 303), from the ether and orthamidophenol; benzenylorthamidothiophenol (benz-

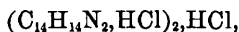


amidophenyl mercaptan, Abstr., 1880, 386), from the ether and orthamidothiophenol; benzenylorthophenylenediamine (m. p.  $280^{\circ}$ ; anhydrobenzoyldiamidobenzene, Abstr., 1881, 1131), from the ether and orthophenylenediamine; and benzenylorthotoluylenediamine (obtained by Hübner from benzometamidoparatoluidide and benzoic chloride, *loc. cit.*) from the ether and orthotoluylenediamine.

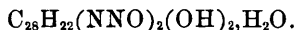
A. G. B.

**Benzylidenimide.** By EDMUND THIELE and HUGO WEIL (*Ber.*, 1895, 28, 1650—1655).—By the reduction of ortho- and para-nitrobenzyl chloride Lellmann and Stickel obtained two bases of the composition  $C_7H_7N$ , which they termed ortho- and para-benzylidenimide, and they ascribed to the latter the constitution  $C_6H_4 < \begin{smallmatrix} NH(1) \\ | \\ CH_2(4) \end{smallmatrix}$ . The authors have been engaged in the examination of this substance, and in view of the paper by Dimroth and J. Thiele (this vol., i, 344), publish the results they have obtained up to the present.

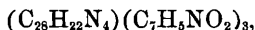
The cryoscopic determination of the molecular weight in phenol solution has shown that the molecular formula of "parabenzylidenimide" is four times as great as that given by Lellmann and Stickel, namely,  $C_{28}H_{28}N_4$ ; it has not yet been obtained in a crystalline condition, but it has been found that under various conditions it takes up the elements of 1 mol.  $H_2O$ . Thus when boiled with formic acid, it yields a *formyl* derivative,  $(C_7H_6N \cdot COH)_4 \cdot H_2O$ , and with acetic acid the corresponding *acetyl* derivative  $(C_7H_6N \cdot Ac)_4 \cdot H_2O$ . Hydrogen chloride in chloroform solution converts it into the compound



which does not yield the free base on treatment with sodium carbonate solution, but a new substance  $(C_7H_7N)_4 \cdot H_2O$ . On treatment with nitrous acid, two of the nitrogen atoms are diazotised, and two combined with nitroso-groups; on boiling, the former are decomposed, and the elements of water simultaneously taken up, with formation of a compound probably of the composition



"Benzylidenimide" combines with paranitrobenzaldehyde in chloroform solution, yielding in the cold an indistinctly crystalline, orange-yellow substance, which sinters at  $175^{\circ}$ , and has the composition



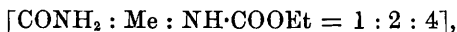
showing that the action has proceeded in the normal manner, each amido-group having combined with 1 mol. of aldehyde, and the two imido-groups with a third. If the chloroform solution be boiled for a long time, this compound takes up the elements of water (obtained from the water formed in the first reaction) yielding the additive compound  $C_{28}H_{22}N_4 \cdot 3C_6H_7NO_2 \cdot H_2O$ , which resembles the foregoing externally but melts at about  $150^{\circ}$ .

The so-called parabenzylidenimide therefore contains two amido- and two imido-groups, and as it forms additive compounds so readily, probably contains an ethylene linkage. The basic groups are probably in the meta-position, as the substance does not combine with

phenanthraquinone or dihydroxytartaric acid. It yields no paratoluidine on reduction, but on distillation with zinc dust, yields aniline in quantity.

H. G. C.

**Derivatives of Metamethylbenzoylorthuramide.** By STEFAN V. NIEMENTOWSKI (*J. pr. Chem.*, 1895, [2], 51, 510—517; compare *Abstr.*, 1889, 1065).—*Carboxethylorthamidoparatoluamide*,



is prepared by mixing orthamidoparatoluamide (m. p. 146°) with ethylic chloroformate, washing the mass with water after it has cooled, and recrystallising from alcohol. It forms long, white needles, melts at 171°, and dissolves in hot alcohol, ether, acetone, chloroform, and benzene, but only sparingly in hot water. When heated above its melting point, it evolves alcohol, and yields metamethylorthouramidobenzoyl, which melts at 317° (*cf. loc. cit.*).

*Nitrometamethylbenzoylorthouramide*, obtained by nitrating metamethylbenzoylorthouramide, crystallises from glacial acetic acid in quadrilateral tables (with 1 mol. acetic acid), or in small prisms. It blackens and melts at 326°, and is either insoluble, or only sparingly so, in most organic solvents; water does not dissolve it. The ammonium and potassium salts are freely soluble. The corresponding amido-compound crystallises in slender, grey needles, blackens and melts at 308°, and is practically insoluble in water and organic solvents; the hydrochloride, nitrate, and sulphate were prepared.

*Dinitrometamethylbenzoylorthouramide* is produced when metamethylbenzoylorthouramide is heated with nitric acid (1.53 sp. gr.) until oxides of nitrogen are no longer evolved, and the cooled liquid poured into ice-cold water. It separates from glacial acetic acid in six-sided crystals, which are active towards polarised light; it melts and decomposes at 294°, but in a capillary tube it melts at 280°; it dissolves in glacial acetic acid and amylic alcohol, but not in other solvents. The ammonium, sodium, and barium salts have been prepared.

The corresponding diamido-derivative forms lilac-grey needles, melts at 333°, and is very sparingly soluble in ethylic and amylic alcohols; dilute ammonia dissolves it, yielding a red solution with a greenish fluorescence. The hydrochloride, nitrate, and sulphate were prepared. The acetyl derivative does not melt below 345°.

A. G. B.

**Derivatives of Anthranil.** By PAUL FRIEDLAENDER and W. SCHREIBER (*Ber.*, 1895, 28, 1382—1386).—Anthranil,  $\text{C}_7\text{H}_5\text{NO}$ , which Friedlaender and Henriques (*Abstr.*, 1883, 187) regarded as the inner anhydride of anthranilic acid, is now shown to be, in all probability, the anhydride of phenylhydroxylamine aldehyde, and to have the constitution  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} > \text{O}$ .

*Dichloranthranil*, ( $\text{Cl}_2 : \text{C} : \text{N} = 1 : 4 : 2 : 3$ ). This was obtained by reducing dichlororthonitrobenzaldehyde (Gnehm, *Abstr.*, 1884, 1028) with tin and acetic acid, and was purified by means of steam distillation. It is only very sparingly soluble in cold water, somewhat more so in hot, and readily in most organic solvents. It

forms small, yellowish needles, and melts at 96—97°. It dissolves in hot dilute mineral acids, and crystallises out unaltered, when the solution is allowed to cool. When warmed with dilute sodium hydroxide it dissolves, and is partially converted into dichloranthranilic acid which melts at 152°.

*Metamethoxyanthranil*.—Metamethoxybenzaldehyde was added to nitric acid (sp. gr. 1.46), which was cooled below 0°. The nitro-aldehyde (m. p. 102°) was separated by means of fractional recrystallisation from benzene, and then reduced in the usual way. The resulting methoxyanthranil is an oil which slowly distils with steam, and has a pleasant aromatic odour. It forms a compound with mercuric chloride, which melts at 185°.

*Methylenedioxyanthranil* was obtained by the reduction of nitropiperonal (m. p. 95.5°). It distils but slowly with steam, and may be obtained from the distillate by the addition of common salt or mercuric chloride. It forms small, white needles, melts at 110.5°; and yields a compound with mercuric chloride; this is insoluble in cold, but readily soluble in hot water, and melts at 238°. When warmed with sodium hydroxide, methylenedioxyanthranil is partially converted into the corresponding *methylenedioxyanthranilic acid* which melts at 203°. J. J. S.

**Glyoxylic acid.** By CARL BOETTINGER (*Arch. Pharm.*, 1895, **233**, 100—104 and 111—118).—When glyoxylic acid (sp. gr. 1.32) is slowly added to a solution of paratoluidine in alcohol and ether a number of products are obtained, the chief of which are paratoluidine acetic acid, paratoluidine acetoparatoluidide, and paratolulylparamethylimesatin. The mixture is allowed to remain over night, the ether and part of the alcohol evaporated, the residue precipitated by the addition of water, and the precipitate thoroughly extracted first with ammonia and then with water. The toluidineacetic acid and tolulylmethylimesatin are thus dissolved, and may afterwards be separated by means of ether, whereas *paratoluidineacetoparatoluidide*,



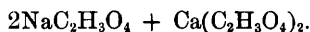
is insoluble, and may be purified by washing with ether, extracting with benzene, and then dissolving in alcohol and precipitating with water. It forms a bright red powder, which is insoluble in cold ammonia and sodium hydroxide, and is decomposed when warmed with these reagents. It is readily soluble in alcohol and in benzene, and is decomposed into paratoluidine, paratoluidineurea, and a substance with an isonitrile smell.

*Paratoluidineacetic acid*,  $\text{C}_7\text{H}_7\text{N}:\text{CH}\cdot\text{COOH}$ , is insoluble in ether and benzene, sparingly soluble in water, but readily in all alkalis. It is also readily soluble in alcohol, and is precipitated on the addition of water in the form of a yellowish, crystalline powder which melts at 193°.

The *paratolulylparamethylimesatin* crystallises from alcohol in golden-yellow plates which melt at 259°. It is sparingly soluble in benzene, but dissolves in concentrated hydrochloric acid, and is thereby converted into paramethylisatin.

In continuation of his work on the condensation of aromatic hydrocarbons with ketonic and aldehydic acids (Abstr., 1881, 1035), the author shows that glyoxylic acid reacts with both benzene and toluene in the presence of concentrated sulphuric acid. The sulphuric acid is covered with a layer of the hydrocarbon, the whole cooled in snow, the glyoxylic acid is added slowly, and the mixture is then thoroughly shaken. Benzene and glyoxylic acid treated in this way yield a small quantity of diphenylacetic acid together with diphenylglycollide and dibenzilic acid. *Diphenylglycollide* is readily soluble in alcohol, chloroform, and ether, but insoluble in water, both hot and cold. It crystallises in small, colourless crystals, melts at  $140^{\circ}$ , and dissolves in warm concentrated sulphuric acid to a yellow solution. Toluene and glyoxylic acid yield *ditolylglycollide* and *ditolyllic acid*. The former separates from ether in large, thin plates, melts at  $131-132^{\circ}$ , and is insoluble in water, but dissolves in ether, alcohol, and chloroform. The *ditolyllic acid*,  $C_{32}H_{30}O_5$ , could not be obtained in a crystalline form; on the addition of a mineral acid to a solution of one of its salts, it separates out in white, flocculent masses. It is insoluble in water, but dissolves in ether, alcohol, and chloroform.

The author also describes a double salt of glyoxylic acid, which was obtained by treating a concentrated neutral solution of sodium glyoxylate with calcium chloride; it has the composition,



J. J. S.

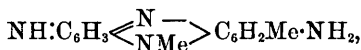
**Constitution of the Fluorindines.** By FRIEDRICH KEHRMANN (*Ber.*, 1895, 28, 1543—1546; compare this vol., i, 148).—The author adduces fresh synthetical evidence in favour of the formula proposed by Fischer and Hepp for the fluorindines, which has been criticised by Nietzki (this vol., i, 477). The products have all been analysed.

*Chlorophenylfluorindine*,  $C_6H_4<\begin{smallmatrix} NH \\ -N \end{smallmatrix}>C_6HCl<\begin{smallmatrix} N \\ -N \end{smallmatrix}>C_6H_4$ , can readily be obtained pure by heating the condensation product of chlorodihydroxyquinone with phenylorthophenylenediamine (which has the formula  $C_6H_4<\begin{smallmatrix} N \\ -N_{Ph} \end{smallmatrix}>C_6H(ClO) \cdot OH$ ), with benzoic acid and orthophenylenediamine hydrochloride. The free base is a crystalline powder with a green, metallic lustre, whilst the *hydrochloride* forms lustrous plates, and is almost insoluble in alcohol.

*Methylphenylfluorindine*,  $C_6H_4<\begin{smallmatrix} NH \\ -N \end{smallmatrix}>C_6HMe<\begin{smallmatrix} N \\ -N_{Ph} \end{smallmatrix}>C_6H_4$ , is prepared in a similar manner from the hitherto undescribed condensation product of phenylorthophenylenediamine with dihydroxytoluquinone. The *hydrochloride* of the fluorindine is formed in almost quantitative amount, and crystallises in long needles with a bronze lustre. The alcoholic solution is deep blue, and is not fluorescent. The base is a lustrous, crystalline powder. This compound is the most readily soluble fluorindine which has hitherto been described. A. H.

**Relations of the Safranines to the Mauveïnes and Indulines.**

By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 1578—1585).—As pointed out by Nietzki (*Ber.*, **28**, 1354), the synthesis of a safranine by the oxidation of a mixture of a metamidodiphenylamine with a paraphenylenediamine may be, in certain cases, expressed by an asymmetrical formula. In some cases, however, this is not possible, and the symmetrical formula must therefore be preferred as being capable of adaptation to all the members of the group. Thus, methylmetatoluylenediamine readily yields a safranine,



when oxidised with paraphenylenediamine, the formula of which cannot be expressed by an asymmetrical formula.

The basicity of the safranines is shown by the solubility in acids of the diacetyl derivative, and is also rendered evident by the electrical conductivity of the solutions of the safranine salts, which behave in a similar manner to those of pararosaniline, methylene blue, and acridine yellow in this respect. It appears, further, that safranine, when pure, is free from water, the amount of water hitherto found in the substance being either water of crystallisation or adventitious moisture.

All these properties of the safranines point to the accuracy of the formula  $\text{HN}:\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{N}^- \\ \text{NR} \end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{NH}_2$ , which was previously proposed for them by the author.

According to this formula, there should only be a monacetyl derivative of safranin, and this appears to be the case, whilst the coloured substance described by Nietzki and Otto (*Abstr.*, 1888, 831) as diacetylsafranin must have some other constitution.

According to the formula proposed, the safranines and mauveïnes must belong to the same class of compounds, and it is probable that these substances are related to induline in the same manner as phenylene red is to eurhodine.

A. H.

**Relationship of Indulines to Safranines.**

By FRIEDRICH KEHRMANN (*Ber.*, 1895, **28**, 1709—1717).—The conversion of aposafranine into the simplest induline of the benzene series observed by O. Fischer and E. Hepp (*Annalen*, **286**, 187) is not in accord with the author's conception of the relationship of these compounds, he has therefore repeated their experiments, which he finds they have incorrectly interpreted; the results confirm his views. Fischer and Hepp state that when heated with aniline, aposafranine hydrochloride,

$\text{C}_6\text{H}_3\text{NH}_2\langle\begin{smallmatrix} \text{N}^1 \\ \text{N}^2\text{ClPh} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , is converted into the hydrochloride of the

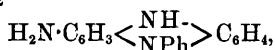
simplest benzene induline,  $\text{NH}:\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{N}^1 \\ \text{N}^2\text{Ph} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , and this, by treatment with alcoholic baryta water and a mixture of glacial acetic and hydrochloric acid, yields benzeneindone and its hydrate respectively,

$\text{O}:\text{C}_6\text{H}_3\text{<}\overset{1}{\text{N}}\text{--}\underset{2}{\text{NPh}}\text{>}\text{C}_6\text{H}_4$  and  $\text{HO}\cdot\text{C}_6\text{H}_3\text{<}\overset{\text{NOH}}{\text{N}}\text{--}\underset{\text{NPh}}{\text{N}}\text{>}\text{C}_6\text{H}_4$ ; they conclude that

indulines and safranines are representatives of different classes of compounds which may be converted into one another by intramolecular rearrangement. The author has been led by his previous investigations to the conclusion that the unoxxygenated induline bases and the indones are paraquinoïdal anhydrides of amido- and hydroxy-azonium bases respectively, and that their salts and hydrates are derived from the orthoquinoïdal azonium form. As the safranines are amido-azonium bases, the confirmation or otherwise of Fischer and Hepp's results must decide the question.

By the action of aniline on aposafranine hydrochloride, in the manner described by Fischer and Hepp, *aniline-aposafranine*,

$\text{HN}^4:\text{C}_6\text{H}_2(\text{NHPh})^5\text{<}\overset{1}{\text{N}}\text{--}\underset{2}{\text{NPh}}\text{>}\text{C}_6\text{H}_4$ , and *hydro-aposafranine*,



are first formed, the latter is then oxidised by the air to aposafranine; the formation of water was clearly recognised. Aniline-aposafranine agrees in properties with Fischer and Hepp's "benzene-induline hydrochloride"; the specimen analysed by them was probably contaminated with dihydrochloride, which is decomposed by water, but is stable in presence of hydrochloric acid. The action of aniline on aposafranine and on quinones is therefore similar in principle. When heated at 160—170° with a mixture of glacial acetic acid and hydrochloric acid, aniline-aposafranine is resolved into aniline and hydroxybenzeneindone (Fischer and Hepp's benzeneinduline, see above),

$\text{O}:\text{C}_6\text{H}_2(\text{OH})^5\text{<}\overset{1}{\text{N}}\text{--}\underset{2}{\text{NPh}}\text{>}\text{C}_6\text{H}_4$ , which is identical with the condensation

product of |dihydroxyquinone and phenylorthophenylenediamine hydrochloride. The position of the aniline radicle in aniline-aposafranine is thus proved. The production of benzeneindone by the interaction of alcoholic baryta water and aniline-aposafranine is probably preceded by the formation of hydroxybenzeneindone, which is then reduced. The oxidation product of orthamidodiphenylamine is isomeric, not identical, with aniline-aposafranine, as it also yields hydroxybenzeneindone by the action of hydrochloric acid, its formula

must be  $\text{NPh}^4:(\text{NH}_2)^5\text{C}_6\text{H}_2\text{<}\overset{1}{\text{N}}\text{--}\underset{2}{\text{NPh}}\text{>}\text{C}_6\text{H}_4$ ; both the base and its salts

closely resemble those of aniline-aposafranine, but it is more feebly basic, and, in ethereal solution, absorbs carbonic anhydride only slowly. It melts at 189—190°; Fischer and Hepp state that it does not melt even at 240°. The hydrochlorides of the two bases differ in crystalline habit, that of aniline-aposafranine being the less soluble. Aposafranine hydrochloride, when heated with dilute soda, readily yields benzeneindone, the compounds therefore bear the same relationship as rosinduline and rosindone.

With aposafranine hydrochloride, paratoluidine reacts like aniline, and forms *paratoluidine-aposafranine*, which crystallises in reddish-brown prisms with a blue sheen; it melts at 219—220°, and dissolves in sulphuric acid with a reddish-violet colour, which does not change on dilution. Solutions of the base are yellowish-red. The *hydrochloride* is deposited in bronze, lustrous prisms; it is more soluble than the corresponding aniline compound, and in this it differs from the base, which is less soluble. When heated with hydrochloric acid and glacial acetic acid at 160—170°, hydroxybenzeneindone, paratoluidine, and ammonia are formed. J. B. T.

**Isomeric Forms of Diacetylthymoquinonoxime.** By E. BÖHM (*Ber.*, 1895, 28, 1547—1549).—*Diacetylthymoquinonoxime* crystallises from light petroleum in two forms, compact needles, and very thin plates with a nacreous lustre. Both of these melt at 110°, but the formation of the plates seems to be favoured by previously heating the solution for some time. The plates are obtained free from needles when iodine is added to the solution in petroleum. The *monacetyl compound* is formed when the diacetyl derivative is heated above its melting point or is treated with iodine in alcoholic solution.

A. H.

**Iodonium Bases from 1 : 2-Iodotoluene.** By M. HEILBRONNER (*Ber.*, 1895, 28, 1814—1816).—These and their salts were prepared as described by V. Meyer and Hartmann (*Abstr.*, 1894, i, 242, 461); the corresponding derivatives from 1 : 4-iodotoluene and from 1 : 4-chloriodobenzene have been already prepared respectively by McCrae and by Wilkinson (this vol., i, 221). The salts described are insoluble, or very sparingly soluble in water; the temperatures given are melting points.

The *base*,  $\text{OH}\cdot\text{I}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}_6\text{H}_3\text{MeI}$ , is only known in aqueous solution. The *iodide* is a yellow powder; the *bromide* a white powder, 162°; the *chloride* a white powder, 162·5°; the *dichromate* a yellow powder, 152°; the *mercuriochloride* a white powder, 137°.

The *base*,  $\text{OH}\cdot\text{I}(\text{C}_6\text{H}_4\text{Me})_2$ , is also only known in aqueous solution. The *iodide*, 152°, forms white needles, turning yellow when exposed to light, and yields 1 : 2-iodotoluene when distilled; the *periodide*, 155°, is decomposed by water and by alcohol. *Bromide*, white needles, 178°. *Chloride*, white needles, 179°. *Dichromate*, yellow needles. *Mercuriochloride*, white plates, 133—134°. *Platinochloride*, flesh-coloured precipitate, or tiny, yellow iridescent needles, 169°. *Aurochloride*, yellow needles, 108°.

C. F. B.

**Dichlorobenzylideneacetone.** By CARL GOLDSCHMIDT (*Ber.*, 1895, 28, 1532).—*Dichlorobenzylideneacetone*,  $\text{CHClPh}\cdot\text{CHCl}\cdot\text{COMe}$ , is prepared by the action of chlorine on benzylideneacetone in chloroform solution; it crystallises in colourless needles and melts at 93°. When treated in alkaline solution with hydroxylamine hydrochloride, *chlorobenzylideneacetoxime*,  $\text{CClPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{NOH}$ , is formed which melts at 133°, and by the action of soda yields a *methylphenylisoxazole*,  $\text{CPh}\cdot\text{CH}\cdot\text{CMe}$   
 $\begin{array}{c} \text{CH}\cdot\text{CMe} \\ \parallel \\ \text{O}-\text{N} \end{array}$ ; this has a neutral reaction, readily dissolves in strong acids, is reprecipitated on dilution, and is volatile with steam.

Attempts to prepare chlorisoquinoline by the action of dehydrating agents on chlorobenzylideneacetoxime were unsuccessful, but when treated with phosphoric anhydride or fuming sulphuric acid, chlorocinnamaldoxime yields a *chlorisoquinoline* which crystallises and melts at  $45^{\circ}$ . The picrate melts at  $177^{\circ}$ . The yield was small.

J. B. T.

**Ionone and Irone.** By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1895, **28**, 1754—1758; compare *Abstr.*, 1894, i, 80).—Ionone readily combines with semicarbazide in acetic acid solution forming *iononesemicarbazone*,  $C_{13}H_{20}\cdot N\cdot NH\cdot CO\cdot NH_2$ , which crystallises from its benzene solution, on the addition of light petroleum, in thin needles melting at  $109$ — $110^{\circ}$ ; it is gradually resolved by mineral acids into ionone and semicarbazone. The isomeric irone also forms a semicarbazone, but this has only been obtained as an oil, which is much more soluble in a mixture of light petroleum and benzene than the foregoing compound.

*Iononeparabromophenylhydrazone*,  $C_{13}H_{20}\cdot N\cdot NH\cdot C_6H_4Br$ , is obtained by the action of parabromophenylhydrazine on ionone in cold acetic acid solution. It is best recrystallised from slightly diluted methylic alcohol, when it forms long characteristic plates which sinter at  $134^{\circ}$  and melt at  $140$ — $145^{\circ}$ ; it is resolved by hydrochloric acid into ionone and parabromophenylhydrazine, the former being recognised by its characteristic odour of violets. When the hydrazone is boiled with acetic acid, it undergoes intramolecular change forming a compound termed by the authors *isoiononeparabromophenylhydrazone*; this crystallises in pale yellow prisms, melts at  $165^{\circ}$ , and is no longer hydrolysed by acids. *Ironeparabromophenylhydrazone*,  $C_{13}H_{20}\cdot N\cdot NH\cdot C_6H_4Br$ , is prepared in a similar manner to the ionone derivative, and forms concentric aggregates of needles which soften at  $156^{\circ}$  and melt at  $168$ — $170^{\circ}$ . When a mixture of ionone and ironeparabromophenylhydrazone is dissolved in warm acetic acid and precipitated by the gradual addition of water, the irone derivative is first deposited, and the two compounds may be separated in this manner.

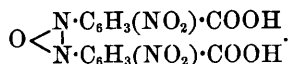
The conversion of both ionone and irone into hydrazone is complete if an excess of the hydrazine is employed, and the reaction may therefore be employed for the quantitative estimation of these substances.

H. G. C.

### Coloured Alkaline Solutions of 1 : 3 : 5-Dinitrobenzoic acid.

—By A. SHUKOFF (*Ber.*, 1895, **28**, 1800—1803).—V. Meyer (this vol., i, 91) has described the variously coloured solutions obtained on dissolving 1 : 3 : 5-dinitrobenzoic acid in an alkali. The first four solutions must contain the original acid, for this is obtained from them when they are acidified; the difference in colour which they exhibit must be due to their containing different salts, normal and basic, of the acid; in some of these, hydrogen atoms of the benzene ring have been replaced by metal. The last, magenta-coloured solution contains two new acids, one of which is precipitated when the solution is acidified, whilst the other remains in solution. The first is a white or brownish powder which decomposes and melts above  $200^{\circ}$ ; it appears to be *dinitroazoxybenzoic acid*,





The second, which is formed in much smaller quantity, is a yellow, amorphous powder; it melts and decomposes below  $200^\circ$ , and its solution in caustic alkalis is magenta coloured; it appears to be an

azoxytrihydroxybenzoic acid,  $\text{O} < \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}(\text{OH})_3 \cdot \text{COOH} \\ \text{N} \cdot \text{C}_6\text{H}(\text{OH})_3 \cdot \text{COOH} \end{array}$

C. F. B.

**Diamidobenzoic acids.** By CARL HAEUSSERMANN and H. TEICHMANN (*J. pr. Chem.*, 1895, [2], 51, 526—528).—Ethylic 3 : 5-diamidobenzoate is best prepared as follows:—A hot solution of ethylic 3 : 5-dinitrobenzoate (9 parts) in alcohol (90 parts) is gradually added to a mixture of tin (15 parts) and hydrochloric acid of sp. gr. 1.19 (30 parts), and the whole is heated on the water bath until the tin has dissolved. Ten times the volume of water is now added, the alcohol is evaporated, and the solution made alkaline with ammonia and shaken with ether. The ethereal solution is dried with caustic soda, the ether distilled, and the residue dissolved in five times its weight of absolute alcohol; to this solution sulphuric acid (1 : 1) is added, and the precipitated sulphate is re-crystallised, dissolved, decomposed with ammonia, and the liberated ethereal salt extracted with ether.

Ethylic 3 : 5-diamidobenzoate melts at  $84^\circ$ ; with hydrochloric acid and a nitrite, it gives the yellow colour characteristic of diamines; when heated with quicklime, it yields calcium carbonate, phenylenediamine, and ethylene. The hydrochloride,  $\text{C}_6\text{H}_3(\text{NH}_2)_2 \cdot \text{COOEt} \cdot 2\text{HCl}$ , sulphate, with  $2\text{H}_2\text{O}$ , picrate and diacetyl derivative (m. p.  $184^\circ$ ) are described.

A. G. B.

**Phenylnitrocinnamic acids and their Stereoisomerides.** By MARUSSIA BAKUNIN (*Gazzetta*, 1895, 25, i, 137—189).—Ortho-, meta-, or para-phenylnitrocinnamic acid may be prepared by heating the corresponding nitrobenzaldehyde with sodium  $\alpha$ -toluate and acetic anhydride in a reflux apparatus for six hours; the solid product of the reaction is extracted with hot water, precipitated with cold water, and the precipitated acid purified by dissolving it in soda and precipitating with hydrochloric acid.

*Phenylorthonitrocinnamic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{COOH}$ , purified by aid of its barium salt, crystallises from alcohol in yellow, anorthic prisms melting at  $195$ — $196^\circ$ ; its sodium salt crystallises in beautiful yellow, anorthic tablets containing  $5\text{H}_2\text{O}$  which is lost at  $80$ — $90^\circ$ . The barium salt crystallises with varying quantities ( $5$  to  $11\text{H}_2\text{O}$ ) of water in efflorescent needles, whilst the sparingly soluble silver salt is obtained as a yellowish precipitate. The methylic salt crystallises in yellow orthorhombic prisms melting at  $75$ — $76^\circ$ , and has the normal molecular weight in freezing acetic acid.

On evaporating the ethereal extract of the mother liquor obtained in the preparation of the foregoing acid, an acid isomeric with it separates; it forms short, monosymmetric, yellow crystals melting at  $146$ — $147^\circ$ . Its silver salt is yellow, and differs in appearance from that obtained from the acid melting at  $195$ — $196^\circ$ ; the methylic salt

crystallises in long, yellow needles melting at 94—95°, and was found to have the normal molecular weight by cryoscopic determinations in acetic acid. The relation between the two acids seems to be the same as that between cinnamic and allocinnamic acids, with the difference, however, that no interconversion of the acids or their methylic salts could be effected.

On attempting to prepare phenylmetanitrocinnamic acid by the above process, a crude mixture of two *isomerides* was obtained which was only purified and separated with difficulty by fractional crystallisation of the very soluble magnesium salts, and fractional crystallisation from alcohol of the acid liberated from the various fractions. One of the acids thus obtained crystallises in yellowish, lustrous prisms melting at 181—182°, and is rather less soluble in alcohol than its isomeride, which crystallises in thin needles melting at 195—196°. The *sodium* salt of the former crystallises in yellowish needles containing 6H<sub>2</sub>O, and the *barium* salt forms lustrous, yellow needles containing 2H<sub>2</sub>O; the *silver* salt is a white powder; the *methylic* salt obtained from it crystallises in long, yellow, monosymmetric prisms melting at 78—79°. The *sodium* salt of the acid melting at 195—196° crystallises in hard, yellow needles; the *barium* salt forms yellow, anorthic prisms containing at least 4½ H<sub>2</sub>O, and the *methylic* salt, prepared from the silver salt, crystallises in yellow, mica-like plates melting at 114—115°.

Two stereoisomeric *phenylparanitrocinnamic acids* can be prepared in a similar manner to the above; one of these crystallises in yellow prisms or needles, and yields a *sodium* salt which forms long, yellow needles containing 4H<sub>2</sub>O, a *barium* salt which crystallises in yellow, monosymmetric tablets containing 1H<sub>2</sub>O, a *silver* salt which forms lustrous, pearly laminæ containing 1H<sub>2</sub>O, and a *methylic* salt which crystallises in yellow, monosymmetric needles melting at 141—142°. The isomeric acid crystallises in orthorhombic, pleochroic, yellow needles melting at 95—105° and containing 1H<sub>2</sub>O which is readily lost giving the anhydrous acid which melts at 140—142°; it crystallises from alcohol with ½ EtOH, and from benzene in beautiful, efflorescent laminæ containing about ¼ C<sub>6</sub>H<sub>6</sub> which melt at about 120° with evolution of benzene. The *sodium* salt crystallises in thin, yellow needles containing at least 3½ H<sub>2</sub>O; the *barium* salt forms needles containing 2H<sub>2</sub>O; the *silver* salt is a yellow powder, and the *methylic* salt melts at 147—148·5°.

On reducing phenylorthonitrocinnamic acid in dilute alcohol with sodium amalgam, *phenylhydrocarbostyryl*,  $\begin{matrix} \text{CHPh} \cdot \text{CO} \\ | \\ \text{CH}_2 - \text{C}_6\text{H}_4 \end{matrix} > \text{NH}$ , is obtained in yellow needles melting at 173—174°; it is accompanied by *phenylorthoamidocinnamic acid*, NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CHPh·COOH, a yellow powder melting at 147—149°, and insoluble in the ordinary solvents.

No well-crystallised substance could be isolated from the reduction product of phenylmetanitrocinnamic acid.

Phenylparanitrocinnamic acid, on reduction with sodium amalgam, yields *phenylparamidocinnamic acid* in microscopic, yellow prisms melting at 200—201°; its *hydrochloride*, C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>·HCl, crystallises

in needles melting at 148—149°, and the *sulphate*,  $(C_{15}H_{15}NO_2)_2 \cdot H_2SO_4$ , is also crystalline, and melts at 220° with decomposition. The amido-acid is converted into *phenylhydroparacoumaric acid*,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CHPh \cdot COOH$ , by the action of nitrous fumes; it crystallises in white laminæ melting at 179—180°, and may also be prepared by reducing phenylparacoumaric acid with sodium amalgam.

W. J. P.

**Crystallography of the Phenylnitrocinnamic acids and their Derivatives.** By EUGENIO SCACCHI (*Gazzetta*, 1895, **25**, i, 310—326).—The author has made a crystallographic examination of many of the compounds recently described in the preceding abstract. No results of theoretical importance have been obtained. W. J. P.

**Constitution of Coumarone.** By GUSTAV KOMPPA (*Ber.*, 1895, **28**, 1643—1644).—The author has already shown (*Abstr.*, 1894, i, 130) that coumarone contains a ring of five members, and has the formula  $C_6H_4 \langle \begin{smallmatrix} CH \\ O \end{smallmatrix} \rangle CH$ . Dennstedt and Ahrens (this vol., i, 475) seem to have overlooked this. C. F. B.

**Intramolecular Rearrangement of Unsaturated Acids. So-called Phenylhydroxycrotonic acid.** By RUDOLPH FITTIG (*Ber.*, 1895, **28**, 1724—1725).—"Phenylhydroxycrotonic acid" is identical with benzoylpropionic acid, as proved by comparison of the salts and of the free acids. Since E. Fischer and Stewart (*Abstr.*, 1892, 1447) have shown that phenylhydroxycrotonitrile has the formula  $CHPh \cdot CH \cdot CH(OH) \cdot CN$ , the treatment with hydrochloric acid must cause an intramolecular rearrangement from



to  $COPh \cdot CH_2 \cdot CH_2 \cdot COOH$ ; of this no explanation can at present be given. Tiemann and Biedermann's statement (*Abstr.*, 1893, i, 471) that, when reduced with sodium amalgam, "phenylhydroxycrotonic acid" yields phenylhydroxybutyrolactone is incorrect; like benzoylpropionic acid, it gives phenylbutyrolactone. J. B. T.

**Quinone-bis-amidobenzoic acid.** By JULES VILLE and CHARLES ASTRE (*Compt. rend.*, 1895, **120**, 878—880).—The acid (this vol., i, 465) dissolves readily in dilute aqueous potash, yielding a red-brown solution, which alters when exposed to air, and from which carbonic anhydride precipitates the greater part of the acid. The potassium salt,  $C_6H_2O_2(NH \cdot C_6H_4 \cdot COOK)_2 + 2H_2O$ , is precipitated in slender needles on adding a mixture of alcohol and ether to the solution; it becomes anhydrous at 100—105°. Its solutions have no reducing action on silver nitrate or Fehling's solution.

The dibenzoyl derivative,  $C_6HCl(OBz)_2(NH \cdot C_6H_4 \cdot COOH)_2$ , is an ochre-yellow substance, insoluble in water and light petroleum, and slightly soluble in other ordinary organic solvents. When heated with dilute sulphuric acid, it yields benzoic acid.

The nitroso-derivative,  $C_6H_2O_2[N(NO) \cdot C_6H_4 \cdot COOH]_2 + H_2O$ , is obtained by the action of sodium nitrite on the acid previously dis-

solved in a mixture of glacial acetic acid (2 parts) and nitric acid (1 part). It is a deep red substance, which loses its water at  $105^{\circ}$ , intumesces at  $180^{\circ}$ , and decomposes when more strongly heated. It is insoluble in light petroleum, almost insoluble in water and benzene, somewhat soluble in alcohol, ether, and chloroform.

Reducing agents seem to convert quinone-bis-amidobenzoic acid into a corresponding quinol derivative, which is very unstable, and has not yet been isolated. It reduces Fehling's solution and ammoniacal silver nitrate.

It would seem that the quinonic function persists in quinone-bis-amidobenzoic acid, and since Knapp has shown that the products of the action of chloroquinones on primary amines are also quinonic, it follows that the constitution of the quinone-bis-amidobenzoic acid is that ascribed to it already.

C. H. B.

**Indole from Orthodiamidostilbene.** By JOHANNES THIELE and OTTO DIMROTH (*Ber.*, 1895, **28**, 1411—1414).—The authors have prepared the two stereoisomeric orthodinitrostilbenes from orthobenzyl chloride and alcoholic potash by Bischoff's method. They find that the two are best separated by recrystallisation from epichlorhydrin and then from ethylic acetate. The *trans*-compound, which is less soluble in epichlorhydrin than the *cis*-, melts at  $191-192^{\circ}$  (Bischoff gives  $196^{\circ}$ ). The *cis*-derivative, after recrystallisation from ethylic acetate, melts at  $126^{\circ}$ . In order to prepare the *trans*-diamidostilbene, the authors recommend the use of stannous chloride and acetic acid saturated with hydrogen chloride as the reducing agents. The *trans*-diamidostilbene, after recrystallisation from benzene, melts at  $168^{\circ}$  (Bischoff,  $176^{\circ}$ ). The *hydrochloride* is sparingly soluble in water, and crystallises with  $2H_2O$ , which it loses at  $100^{\circ}$ .

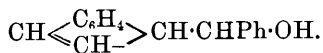
The *cis*-diamidostilbene was prepared in a similar manner from the *cis*-dinitro-compound. It forms small red needles, and melts at  $123^{\circ}$ . The *hydrochloride*, which was obtained as a greyish powder by precipitating the ethereal solution of the base with hydrogen chloride, melts at  $230^{\circ}$ .

In order to obtain a good yield of indole, a mixture in molecular proportions of the *trans*-diamidostilbene and its dihydrochloride is distilled for about three-quarters of an hour at  $170-185^{\circ}$  in a vacuum. The monohydrochloride is the first product formed, and this is then decomposed into indole and aniline hydrochloride. This latter then reacts with a further quantity of the diamidostilbene hydrochloride, forming aniline and the dihydrochloride of the diamidostilbene. Thus at the end of the reaction all the free base which was present at the beginning has passed over in the form of indole and aniline, whereas the dihydrochloride remains behind in the retort in a pure state. The distillate is then acidified, saturated with common salt, and subjected to steam distillation, whereby the indole passes over in almost theoretical quantity.

*Cis*-diamidostilbene also yields indole when heated, but as it is more difficult to obtain in large quantities, it is not so useful a source for indole as the *trans*-compound.

J. J. S.

**Constitution of Indene.** By WILLY MARCKWALD (*Ber.*, 1895, **28**, 1501—1505).—With benzaldehyde, indene readily forms a condensation product which separates from alcohol in yellow crystals, and melts at 135°. This substance is *hydroxybenzylindene*,



The *acetate* crystallises in orange-yellow prisms, melting at 110—111°. When indene is treated with amyl nitrite and sodium ethoxide, an isonitroso-compound is formed as a reddish-yellow oil, which is readily soluble in alkalis, but has not yet been obtained pure.

Methylindene reacts in a similar manner both with benzaldehyde and amyl nitrite, but the products of the action have not been obtained pure. Neither hydrindene nor coumarone undergo either of these changes.

This remarkable behaviour of the methylene group of indene is probably due to the acidifying effect of its position in a ring of five atoms, and is a further argument in favour of the analogy of indene and methylindene to indole, and against the formula for indene proposed by Dennstedt and Ahrens (this vol., i, 475). A. H.

**$\beta$ -Metatolyl- $\alpha$ -diketohydrindene.** By EDUARD BRAUN (*Ber.*, 1895, **28**, 1388—1393).—When xylylidene-phthalide (Heilmann, *Abstr.*, 1890, 625) is suspended in alcohol and heated during an hour with sodium methoxide, it is converted into the *sodium derivative of tolyldiketohydrindene* (compare *Abstr.*, 1893, i, 415), which crystallises from water in red needles. When an aqueous solution of the sodium derivative is warmed with acids, the red colour disappears, and the *meta-tolyldiketohydrindene* itself,  $\text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_3$ , separates; this crystallises in white plates, and melts at 134—135°. It is insoluble in water, but readily soluble in most other solvents. It dissolves in alkalis, yielding a yellow solution, from which it is precipitated unaltered on the addition of acids. The *phenylhydrazone* crystallises in long, yellow needles, melts at 167—168°, is soluble in benzene and toluene, and dissolves in concentrated sulphuric acid yielding a dirty green solution. The *dioxime* is obtained on warming the diketone with hydroxylamine hydrochloride and sodium hydroxide in dilute alcoholic solution until the colour changes from red to yellow; it forms colourless crystals, which decompose at 222°, and is sparingly soluble in benzene, but readily in methylic and ethylic alcohols.

*Tolylbromodiketohydrindene*,  $\text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{CBr} \cdot \text{C}_6\text{H}_3$ , is obtained by brominating the diketone; it crystallises in colourless plates, melts at 88°, and does not show the acid reactions of the diketone. The corresponding *chloro-derivative*,  $\text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{CCl} \cdot \text{C}_6\text{H}_3$ , crystallises from alcohol in colourless plates, which melt at 92—93°.

*Tolyldiketohydrindeneanilide*,  $\text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{C}(\text{NHPh}) \cdot \text{C}_6\text{H}_3$ , obtained by warming the bromo- or chloro-derivative with aniline, crystallises in yellow needles, and melts at 171°.

*Tolylbenzoyldiketohydrindene*,  $\text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{CBz} \cdot \text{C}_6\text{H}_3$ , is obtained when the diketone is heated with an excess of benzoic chloride and

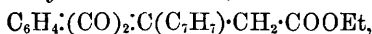
then boiled with dilute sodium hydroxide. It crystallises in yellowish-red needles, and melts at 112—113°.

*Phenylbenzoyldiketohydrindene*,  $C_6H_4:(CO)_2:CBz \cdot Ph$ , was prepared by treating phenyldiketohydrindene (Abstr., 1894, i, 37) with benzoic chloride. It crystallises from benzene in small, yellow prisms, and melts at 168°. Tri-oximes corresponding with the last two compounds could not be obtained.

*Methyltolylldiketohydrindene*,  $C_6H_4:(CO)_2:CMe \cdot C_7H_7$ , is formed when a solution of the sodium salt of the diketone in methylic alcohol is heated with excess of methylic iodide. It crystallises in colourless plates, and melts at 97°.

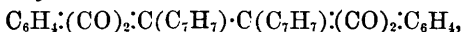
The *ethyltolylldiketohydrindene* melts at 63—65°, and is readily soluble in most solvents except light petroleum.

*Ethylic tolyldiketohydrindene acetate*,



obtained by the action of ethylic monochloracetate on the sodium derivative of the diketone at 100°, crystallises from methylic alcohol in colourless, quadratic plates, and melts at 116—118°.

*Bistolyldiketohydrindene*,



is obtained when the diketone is oxidised with nitrous acid. It crystallises in small, white needles, and melts at 203—205°.

*Benzylphenyldiketohydrindene*,  $C_6H_4:(CO)_2:CPh \cdot CH_2Ph$ , obtained by the action of benzylic chloride on the sodium derivative of phenyldiketohydrindene, forms colourless crystals, and melts at 105—106°.

*Cyanometaxylylidenephthalide*,  $CO < \begin{smallmatrix} C_6H_4 \\ -O- \end{smallmatrix} > C:C(CN) \cdot C_7H_7$ , is formed when equal quantities of metatolylacetonitrile and phthalic anhydride are heated with a small quantity of sodium acetate; it forms lemon-yellow needles, which melt at 144—145°. When treated with sodium ethoxide, it is not converted into a diketo-compound. It yields a *dinitro-derivative*,  $C_{17}H_9N(NO_2)_2O_2$ , when added to fuming nitric acid; this separates from benzene in yellow crystals, which melt at 187—188°.

J. J. S.

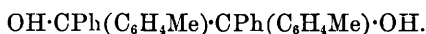
**Synthesis of Indigo from Ethylenedianthranilic acid.** By J. FRÄNKEL and KARL SPIRO (*Ber.*, 1895, **28**, 1685—1688).—When ethylic anthranilate (4 mols.) is heated with ethylenic bromide (1 mol.) at 140—160°, *ethylic ethylenedianthranilate*,



is formed and remains as a solid substance on treating the product with water and dilute hydrochloric acid. It crystallises from alcohol in needles melting at 117°, and is readily hydrolysed by warming with alcoholic potash. The free *ethylenedianthranilic acid* is scarcely soluble in water and only sparingly in the other neutral solvents, and crystallises from nitrobenzene in indistinct crystals, melting at 213—214°. The constitution of the acid is closely allied to that of indigo, and attempts were therefore made to convert it into the latter. The ordinary condensation agents were without effect,

but when fused with caustic potash in absence of air, according to Heumann's method, it yields a yellow mass, containing a leuco-compound which is soon converted into indigo by the oxygen of the air. The yield is, however, small. H. G. C.

**Preparation of Pinacones by the Reduction of Aromatic Ketones.** By K. ELBS and K. SCHMITZ (*J. pr. Chem.*, 1895, [2], 51, 591—592).—The ketone was dissolved in glacial acetic acid, twice the calculated quantity of zinc dust was gradually added and the whole warmed on the water-bath until the zinc was almost entirely converted into acetate. By this treatment (1) acetone, phenyl-ethyl methyl ketone, and dibenzyl ketone, remained unchanged; (2) acetophenone yielded the pinacone,  $\text{OH}\cdot\text{CMePh}\cdot\text{CMePh}\cdot\text{OH}$ ; (3) benzophenone yielded benzopinacone,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CPh}_2\cdot\text{OH}$ ; (4) phenyl paratolyl ketone yielded the pinacone,



Pinacones were also obtained in this way from phenyl metaxylyl ketone, phenyl pseudocumyl ketone, phenyl  $\alpha$ -naphthyl ketone, and, particularly easily from parahydroxybenzophenone, parethoxybenzophenone, and parahydroxybenzophenone benzoate.

A. G. B.

**Orthophenobenzylamine and Cyclophenylenbenzylidene Oxide.** By PAUL COHN (*Monatsh.*, 1895, 16, 267—282).—The author has previously described the preparation of phenylorthocresolamine,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{NH}_2$ , by the reduction of an alcoholic solution of phenylindoxazene with sodium, and on account of its close relation to orthobenzylphenol suggests for it the more appropriate name of orthophenolbenzylamine (compare this vol., i, 371). This base yields a *dibenzoyl* derivative,  $\text{C}_{27}\text{H}_{21}\text{NO}_3$ , which is insoluble in acids and alkalis, and an *ethyl* derivative which when freshly prepared is an oil, but gradually assumes the solid form. The latter gives a well-characterised hydrochloride and an orange-red, crystalline platinochloride,  $(\text{C}_{15}\text{H}_{17}\text{NO})_2\cdot\text{H}_2\text{PtCl}_6$ . Orthophenolbenzylamine acts as a powerful poison, is optically inactive, loses ammonia at  $130$ — $150^\circ$  and when heated with dilute hydrochloric acid, first for 3—4 hours at  $130$ — $140^\circ$ , and afterwards for an equal time at  $150^\circ$ , is resolved into ammonia and *cyclophenylenebenzylidene oxide*,  $\text{C}_6\text{H}_4\cdot\text{C}(\text{CHPh})_2\text{O}$ . The latter, which is obtained in 90 per cent. of the

theoretical yield, crystallises from benzene in small, yellow, monoclinic needles, is insoluble in mineral acids, but dissolves readily in acetic acid or alcohol, and also in alkalis forming a brown solution. It softens at  $170^\circ$ , and when heated to a slightly higher temperature rapidly blackens. At  $210^\circ$ , it forms a dark-coloured, viscid liquid. The *benzoyl* derivative,  $\text{C}_{13}\text{H}_5\text{BzO}$ , is a yellow, crystalline powder, which sinters at  $150^\circ$ , simultaneously darkening, and at  $190^\circ$  becomes a thick, greasy mass. It is insoluble in acids, alkalis, alcohol, and petroleum, but dissolves in chloroform. The *ethyl* derivative,  $\text{C}_{13}\text{H}_{14}\text{O}$ , forms slender crystals, softens at  $150^\circ$ , and becomes a viscid, brown oil at  $168$ — $170^\circ$ . The *acetyl* derivative,  $\text{C}_{13}\text{H}_9\text{AcO}$ , crystallises

from acetic acid in slender, white needles, softens and becomes yellow at  $180^{\circ}$ , and at  $190^{\circ}$  exists as a viscid, transparent fluid. The *sodium* derivative,  $C_{13}H_9NaO$ , is a brown powder which readily dissolves in water, to which it gives alkaline properties. G. T. M.

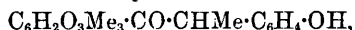
### The Reducing Action of Alcohol at High Temperatures.

By WILHELM KERP (*Ber.*, 1895, **28**, 1476).—Ethylic alcohol and amylic alcohol reduce benzophenone to benzhydrol when they are heated with it at  $300$ – $320^{\circ}$ , the alcohols being converted into the corresponding aldehydes. The same reaction occurs with ethylic alcohol and diphenyleneketone, acetophenone, phenanthraquinone and anthraquinone. No action appears to take place at lower temperatures, and no aldehyde is formed when alcohol is heated by itself to  $340^{\circ}$ . A similar action has been observed with sodium ethoxide, at  $200^{\circ}$ , by Haller and Minguin (*Compt. rend.*, **120**, 1105). Methylic alcohol does not appear to react in this way. A. H.

### Constitution of Maclurin and Phloretin.

By GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1895, **28**, 1393–1398); compare Abstr., 1894, i, 471. From their own observations, and from those of König and v. Kostanecki (Abstr., 1894, i, 534), the authors think maclurin is to be regarded as 2:4:6:3':4'-pentahydroxybenzophenone, and the condensation product obtained by the action of acetic anhydride and anhydrous sodium acetate as the tetracetyl derivative of tetrahydroxyphenylcoumarin. It is shown that maclurin is closely related to the cotoines, cotogenin, protocotoin and oxyleucotin.

The substance described by Mrs. Michael (this vol., i, 45) as triacetylphloretin is shown to be a tetracetyl derivative of phloretin. A *trimethylphloretin* is obtained when phloretin is heated with methylic iodide and methylic alcoholic potash; it has the constitution



and forms pale yellow plates which melt at  $152^{\circ}$ . When the mother liquor from this trimethyl derivative is evaporated, and the residue again treated with methylic iodide, a new substance, having the composition  $C_{19}H_{22}O_5$ , is obtained. This forms yellowish plates which melt at  $58^{\circ}$ . It is the methyl ether of the above mentioned trimethylphloretin, since it yields the latter when treated with hydriodic acid. J. J. S.

### Phthalein-melts.

By R. von ROTHENBURG (*J. pr. Chem.*, 1895, [2], **51**, 578–580).—The author draws a comparison between the production of fluoresceins, rhodamines, pyronines, and fluoramines.

A. G. B.

### Constitution of Fluorescein. Ethereal Salts and Mixed

**Anhydride of Phthalic Acid.** By RICHARD MEYER (*Ber.*, 1895, **28**, 1576–1577).—Heller has shown (this vol., i, 234) that one of the hydroxyl groups of fluorescein is in the para-position with respect to the carbonyl group. That the second hydroxyl group also occupies the para-position follows from the following facts. When dibromodihydroxybenzoylbenzoic acid,  $COOH \cdot C_6H_4 \cdot CO[C_6HBr_2(OH)_2]_2$ , obtained by the action of an alkali on eosin, is heated above its melting point, it

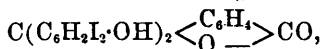


yields phthalic acid which sublimes, and eosin; the latter is identical with the ordinary colouring matter in every respect. It follows from this that eosin, and, therefore, fluorescein itself must have the symmetrical constitution.

The ethereal salts obtained by acting on silver phthalate with benzylic iodide, and on sodium benzyloxide with phthalic chloride are identical. The same is true of the mixed anhydrides prepared from phthalic chloride and silver benzoate, and from benzoic chloride and silver phthalate.

A. H.

**Action of Iodine on Phenolphthaleïn.** By ALEXANDER CLASSEN and WALTHER LÖB (*Ber.*, 1895, 28, 1603—1611).—Phenolphthaleïn is converted by iodine into *tetraiodophenolphthaleïn*,



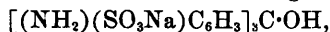
which forms yellowish, granular crystals, and decomposes at about 220° without melting. It is readily soluble in alkalis, forming salts of tetraiodophenolphthaleïncarbinolcarboxylic acid, from which the free acid,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{I}_2\cdot\text{OH})_2$ , may be obtained by careful acidification at -5°. The latter is a yellowish-brown substance which is converted into tetraiodophenolphthaleïn at 100°. The *sodium salt* forms a blue mass and is soluble in water, in which tetraiodophenolphthaleïn itself is insoluble. The *barium salt* is a greyish-blue powder, whilst the salts of most of the heavy metals are brown.

Tetraiodophenolphthaleïn acts as a strong antiseptic in the animal organism, through which it appears to pass unchanged.

The preparation of the compound may be carried out by dissolving phenolphthaleïn in alkali or baryta water and adding iodine, by which means the corresponding salt is obtained. The substance itself, and not the sodium salt, is formed when phenolphthaleïn is dissolved in borax or sodium phosphate solution and treated with iodine, or when a solution of phenolphthaleïn in alkaline potassium iodide solution is submitted to electrolysis.

A. H.

**Sulphonated Colouring Matters of the Triphenylmethane Series.** By MAURICE PRUD'HOMME (*Chem. Centr.*, 1895, i, 41; from *Bull. Soc. Ind. Mulhouse*, 1894, 403—407).—The author criticises Rosenstiehl's view that the rosanilinesulphonic acids exist in three forms; the colourless modification of acid magenta,



is really the dye-stuff, since it contains the acid phenolic group; Rosenstiehl's supposition that a form derived from this by substituting chlorine for the hydroxyl group constitutes the colouring matter, is therefore unnecessary.

The decolorisation of patent blue can hardly be due to the conversion of the  $\text{:C}\cdot\text{OH}$  group into the group  $\text{:C}\cdot\text{ONa}$ , for then the colour should reappear on acidification immediately, instead of requiring several days in the cold; the colourless compound is most likely a condensation product of two molecules of the coloured one.

W. J. P.

**Constitution of Acid Magenta.** By AUGUSTE ROSENSTIEHL (*Chem. Centr.*, 1895, i, 41—42; from *Bull. Soc. Ind. Mulhouse*, 1894, 408—413).—The author combats the views of Prud'homme (see preceding abstract) on acid magenta. W. J. P.

**Constitution of the Rosanilines.** By ARTHUR MIOLATI (*Ber.*, 1895, 28, 1696—1701).—The electrolytic conductivity of pararosaniline, as previously given by the author (*Abstr.*, 1893, i, 572), is only half the true value, owing to an error in the calculation. The following additional determinations have been made at 25°.

	$v =$	128.	256.	512.	1024.
Pararosaniline .....	$\mu =$	84.24	87.29	91.28	93.27
Phenosafranine.....	$\mu =$	79.41	81.69	82.61	83.13
Methylene blue.....	$\mu =$	88.97	93.56	95.76	96.60
Leucaniline trihydrochloride	$\mu =$	343.9	382.4	419.9	465.3
Hydrocyanopararosaniline trihydrochloride .....	$\mu =$	361.2	419.9	478.2	539.5
Pararosaniline + HCl.....	$\mu =$	291.7	327.0	374.9	399.1
„ + 2HCl ....	$\mu =$	454.8	513.6	579.4	651.6
„ + 3HCl ....	$\mu =$	700.3	753.7	891.4	921.1
Hexamethylpararosaniline hydrochloride (crystal violet).....	$\mu =$	78.0	81.60	83.88	84.71

The conductivity of pararosaniline may be dependent on the presence of amido-groups, as Rosenstiehl suggests, or may be due to its being a true salt, in the former case it should be resolved into the ions,  $C_{19}H_{19}N_3Cl$  and  $OH$ , in the latter into  $C_{19}H_{18}N_3$  and  $Cl$ . The maximum conductivity calculated for the first hypothesis = 190, for the second = 93.2, the close agreement of this value with the experimental results, and the analogy shown to phenosafranine and methylene blue, prove that pararosaniline is a true salt; confirmation of this is afforded by the great difference in behaviour between pararosaniline in hydrochloric acid solution, leucaniline trihydrochloride, and hydrocyanopararosaniline trihydrochloride solutions. Haller and Müller have stated that pararosaniline and crystal violet do not dissociate in aqueous solution; the author is unable to confirm this, his molecular weight determinations of the former, by the boiling point method, give values ranging from 144.8—186 (cal. = 323.7); the electrolytic conductivity of the latter is given above. By the action of hydrogen chloride on leucaniline, suspended in alcohol, a somewhat unstable compound,  $C_{19}H_{19}N_3 \cdot 4HCl + H_2O$ , is obtained; the formation of this is incompatible with Rosenstiehl's formula, which is also not in accordance with the spectroscopic properties of pararosaniline salts; these, as Ostwald has shown, have identical absorption spectra. (Compare following abstract.)

J. B. T.

**Constitution of Rosanilines.** By M. TORTELLI (*Ber.*, 1895, 28, 1702—1707).—The haloids are completely precipitated from pararosaniline and its analogues by means of silver nitrate, in presence of nitric acid. The following compounds were examined—hydrated and

anhydrous pararosaniline, pararosaniline iodide, and "crystal violet." Barium chloride completely precipitates the sulphur of pararosaniline sulphate and "brilliant green." Full details of the experiments are given in the paper. The electrolytic conductivity of the following compounds, which resemble the ordinary pararosaniline salts, has also been determined.

	$v =$	256.	512.	1024.
Pararosaniline sulphate ( $C_{19}H_{16}N_3$ ) <sub>2</sub> , $H_2SO_4 + 8H_2O$ .....	$\mu =$	83·39	85·12	86·26
Pararosaniline iodide, $C_{19}H_{16}N_3HI$ .	$\mu =$	—	88·03	90·07

Müller's hydrocyanopararosaniline,  $NC \cdot C(C_6H_4 \cdot NH_2)_3$ , is formed by the action of barium cyanide on pararosaniline sulphate, and of ammonium cyanide or hydrogen cyanide on the free base. When boiled with mercuric cyanide, in dilute alcoholic solution, pararosaniline yields a compound  $C_{19}H_{17}N_3 \cdot HCl \cdot Hg(CN)_2$ , which crystallises in small, thin needles with a greenish metallic lustre, and is sparingly soluble. The corresponding *chloride*,  $C_{19}H_{17}N_3 \cdot HCl \cdot HgCl_2$ , crystallises in slender plates. By the interaction of mercuric cyanide, pararosaniline, and hydrogen cyanide at  $0^\circ$ , two compounds are formed, the one,  $C_{19}H_{17}N_3 \cdot HCN \cdot Hg(CN)_2$ , crystallises in green plates with a bronze reflex. The second substance,  $2C_{19}H_{17}N_3 \cdot HCN \cdot Hg(CN)_2$ , obtained in larger quantity, is a greenish-red crystalline powder. When boiled with water, both compounds are resolved into hydrocyanopararosaniline, but they are not formed from this compound by the action of mercuric cyanide. When treated with hydrogen sulphide, mercury is eliminated from all the above double cyanides, but the solution retains the characteristic magenta colour; on evaporation, a green, crystalline compound is formed, which decomposes into the cyanopararosaniline, when attempts are made to purify it. The substance is probably the coloured cyanide corresponding with the ordinary salts of pararosaniline. The compound,  $C_{19}H_{17}N_3 \cdot HCN \cdot HgCl_2$ , formed from pararosaniline, mercuric chloride, and hydrogen cyanide at  $0^\circ$ , is more stable than the corresponding cyanide, and is deposited in long, green, lustrous crystals. The formation of the above compounds, and the behaviour of the haloïd salts of pararosaniline, can not be explained by Rosenstiehl's pararosaniline formula (compare preceding abstract).  
J. B. T.

**Oxidation Products of Tetramethyldiamidodiphenylcarbinol.** By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], 13, 273—275).—Tetramethyldiamidodiphenylcarbinol,



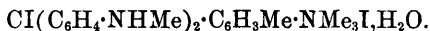
is oxidised by sulphuric acid at  $125^\circ$  to the corresponding ketone, but by lead peroxide in presence of hydrochloric acid to tetramethylbenzidine,  $NMe_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_2$ , with elimination of carbonic anhydride. A noteworthy point in the latter oxidation is the stability of the dimethylamidophenyl groups.  
JN. W.

**Instability of Tetramethyldiamidodiphenylcarbinol.** By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], 13, 275—277).—

The author confirms his previous results, and in commenting on the subsequent results obtained by Weil (this vol., i, 145), shows that the decomposition of this carbinol by acids into hexamethyltriamidotriphenylmethane and paradimethylamidobenzaldehyde is practically quantitative, and takes place to a certain extent even in the cold, and in dilute solutions.

JN. W.

**Iodine Green.** By LÉON LEFÈVRE (*Bull. Soc. Chim.* 1895, [3], 13, 247—252).—In dyes of the rosaniline type, the effect on the colour produced by neutralising a para-amido-group is the same as that of eliminating it, violet becoming green, and green red. As this first colour change takes place in the formation of iodine green from the violet-red colouring matter,  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}$ , the methylic iodide must have transformed an amido into an ammonium group, and the constitution of the green dye must therefore be



A substance having this constitution would, as Hofmann found, readily lose water and methylic iodide, and the product of this decomposition would have the constitution  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2$ , and, therefore, be bluer in tinge than the corresponding trimethyl compound, as is the case. The composition and constitution usually assigned to iodine green by analogy with hexamethylpararosaniline, namely,  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_3\text{I}$ , do not account for the formation of a violet colouring matter having the above composition, and, moreover, are not in accordance with Hofmann's analytical data.

In accordance with these views, the violet colouring matters prepared by Hofmann and Girard by heating iodine green with methylic alcohol, would have the constitutions



and  $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NHMe})\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2$ , respectively, and the colourless product obtained at the same time, the constitution



JN. W.

**A Synthesis of Unsaturated Aromatic Acids.** By GEORG HEYL and VICTOR MEYER (*Ber.*, 1895, 28, 1798—1799).—*Triphenylacrylonitrile*,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{CN}$ , can be obtained by heating benzophenone chloride,  $\text{CPh}_2\text{Cl}_2$ , with benzylic cyanide in an open vessel until the evolution of hydrogen chloride ceases; it crystallises in needles and melts at  $162$ — $163^\circ$ . It cannot be hydrolysed to the acid in the usual manner: prolonged boiling with alcoholic potash, however, converts it into the *amide*, melting at  $223^\circ$ , and this can be further converted into the *acid* by treatment with sodium nitrite and sulphuric acid. The acid may also be prepared by heating benzophenone chloride with ethylic phenylacetate, and hydrolysing the ethylic salt thus obtained with alcoholic potash; it crystallises in needles, and melts at  $212$ — $213^\circ$ .

C. F. B.

**Triphenylthienylmethane.** By KARL WEISSE (*Ber.*, 1895, **28**, 1537—1538).—*Triphenylthienylmethane*,  $C_4SH_3 \cdot CPh_3$ , is prepared by heating triphenylcarbinol and thiophen with phosphoric anhydride; it crystallises from a mixture of benzene and light petroleum in needles or large prisms, melts at  $239^\circ$ , and boils at  $433\text{--}438^\circ$  (corr.), a small portion being decomposed. The yield is quantitative. The formation of this compound shows that the failure of all attempts to prepare tetraphenylmethane is due either to the comparatively great stability of benzene or to its own instability, and not to any stereochemical cause, since the volume occupied by the thienyl and phenyl groups is practically equal. J. B. T.

**Oxidation of Nitronaphthalene.** By PAUL FRIEDLAENDER and J. WEISBERG (*Ber.*, 1895, **28**, 1641—1643).—When nitronaphthalene is oxidised by boiling with aqueous permanganate solution, and the filtrate reduced with ferrous sulphate, ethylic acetate extracts two substances from the colourless solution thus obtained. That one which first crystallises appears to be *isatincarboxylic acid*,  $C_9H_5NO_4$ ; it turns brown above  $200^\circ$ . It yields a *barium salt* in yellow needles, and the solution of this salt is turned cherry-red by the addition of baryta water; on warming, the colour changes to pale yellow, and the addition of acids also restores the original reddish-yellow colour. The acid can further be converted into indopheninecarboxylic acid, and also into indigocarboxylic acid. C F. B.

**Reaction of 1 : 3 : 1'-Nitronaphthalenedisulphonic acid.** By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1535—1537).—1 : 3 : 1'-Nitronaphthalenedisulphonic acid is formed from 1 : 3'-naphthalenedisulphonic acid, and is employed for the technical preparation of 1 : 3 : 1'-naphtholdisulphonic acid (*c*-acid). The *potassium salt*,  $C_{10}H_5NO_4(SO_3K)_2$ , and the *calcium salt* crystallise in yellow needles; the *barium salt* is deposited in flat, stellate needles; the *zinc salt* in long, thin, almost colourless, crystals; the *lead* and *copper* salts have also been prepared, all are readily soluble. When carefully heated with soda, the above potassium salt is converted into the basic sodium salt of 1-nitroso-4-naphthol-3 : 1'-disulphonic acid, which crystallises in slender, greenish, lustrous needles; the *potassium salt*,



is deposited in small, yellow, stellate needles; the *basic potassium salt* forms green needles, the *basic* and *neutral calcium* and *barium salts* also crystallise in needles; all are readily soluble. When reduced the above compound is converted into 1 : 4-amidonaphthol-3 : 1'-disulphonic acid, which crystallises in colourless needles, can not be diazotised, does not combine with diazo-compounds, and, in alkaline solution, turns green when exposed to air. The *silver salt* is pale yellow and insoluble; the *potassium*, *barium*, and *copper salts* are readily soluble. By the action of sodium amalgam on the above acid in neutral or slightly acid solution, one sulphonic group (probably that in the 1 position) is eliminated, the resulting compound crystallises in silvery, lustrous plates, and, when further reduced, yields

1:4-amidonaphthol. The formation of the nitrosonaphthol resembles the intramolecular rearrangement which occurs in the case of phenylhydroxylamine derivatives; none of the isomeric nitronaphthalene-sulphonic acids that have hitherto been investigated undergo a similar change. J. B. T.

**Constitution of  $\beta$ -Anthraquinone.** By KASIMIR LAGODZINSKI (*Ber.*, 1895, 28, 1422—1424).—The  $\beta$ -anthraquinone (*Abstr.*, 1894, i, 420) obtained by the author from 2-hydroxyanthracene was previously shown to be an orthoanthraquinone, and is now shown to be the 1:2-anthraquinone.

When the nitroso-derivative of 2-hydroxyanthracene is treated in alkaline solution with hydrogen sulphide, free *amidohydroxyanthracene* is obtained; this, on recrystallisation from ether, forms greenish-yellow plates, which, when quite pure, are not decomposed on exposure to the air. They darken at  $140^\circ$ , and decompose at  $150^\circ$ . A *triacetyl derivative*,  $\text{OAc}\cdot\text{C}_{14}\text{H}_8\cdot\text{NAc}_2$ , was prepared by warming the amidohydroxyanthracene for a short time with acetic anhydride; after recrystallisation from dilute alcohol, it forms large, slightly fluorescent plates, which melt at  $164^\circ$ . When oxidised with chromic acid, it yields *triacetylamidohydroxyanthraquinone*,  $\text{OAc}\cdot\text{C}_{14}\text{H}_6\text{O}_2\cdot\text{NAc}_2$ , which crystallises from benzene in bright yellow, flat prisms, and melts at  $181^\circ$ . This triacetyl compound may be hydrolysed by prolonged boiling with a solution of sodium hydroxide; when the blood-red solution thus obtained is acidified, a deep red precipitate of hydroxy-amidoanthraquinone is thrown down. This compound is identical with the alizaramide of Liebermann (*this Journal*, 1877, i, 613), which has the constitution 1:2-amidohydroxyanthraquinone. It therefore follows that the original hydroxyamidoanthracene is 1:2-amidohydroxyanthracene. As the  $\beta$ -anthraquinone is obtained by the oxidation of this 1:2-amidohydroxyanthracene, it follows that it is the 1:2-anthraquinone. J. J. S.

**2:3-Dihydroxyanthracene.** By KASIMIR LAGODZINSKI (*Ber.*, 1895, 28, 1533—1535).—2:3-*Dimethoxyanthracene* is readily prepared by the action of zinc dust and dilute ammonia on hystazarin dimethyl ether (*this vol.*, i, 232); it crystallises from petroleum in colourless plates, melts at  $203$ — $204^\circ$ , and, in alcoholic solution, exhibits a fluorescence similar to that of anthracene, which it resembles in appearance. The yield is quantitative. The compound sublimes when slowly heated; in solution, it gradually changes both in melting point and appearance, polymeric compounds being probably formed. The *picrate* is dark brown, and readily soluble.

2:3-*Dihydroxyanthracene*, formed by the action of hydriodic acid on the preceding compound, is deposited with some difficulty in pale yellow, ill-developed crystals; it chars without melting, and dissolves in sulphuric acid with a brownish-red coloration; when heated, the colour changes to dull green, then to blue. The compound is not oxidised by heating with ferric chloride, platinum tetrachloride, gold chloride, or chromic acid, boiling dilute nitric acid decomposes it, but is without action at the ordinary temperature; the product

formed by treatment with potassium ferricyanide was ill defined; this indicates that the substance is a diphenol, not a quinol, and that the carbon atoms 2:3 are probably singly linked. The *diacetyl derivative* is deposited in small, pale yellow, concentric crystals, melting at 160°. In solution, it shows a faint fluorescence, resembling that of anthracene.

J. B. T.

**Synthesis of Alizarin from Hemipinic acid.** By KASIMIR LAGODZINSKI (*Ber.*, 1895, **28**, 1427—1429).—The author has previously shown (*Ber.*, **27**, 116) that when phthalic anhydride is treated according to Friedel-Craft's method with an ether of quinol or of catechol, the products are respectively quinizarin and hystazarin. The action of benzene on hemipinic acid in the presence of aluminium chloride has since been studied; the product obtained by decomposing the resulting aluminium compound with hydrochloric acid crystallises in long, colourless needles, and melts at 86—87°; it has the composition  $C_{15}H_{12}O_3 + H_2O$ , and is probably a *hydroxymethoxybenzoylbenzoic acid*, its formation being due to the hydrolysis of one of the methoxy-groups of hemipinic acid by the aluminium chloride. It dissolves in cold concentrated sulphuric acid, yielding a yellowish-red solution with a yellowish-green fluorescence. If this solution is heated to 100°, the colour changes to dark red and then to violet; when the latter solution is poured on to ice, a precipitate of a monomethyl ether of alizarin is obtained. This ether crystallises from glacial acetic acid in long, glistening, reddish-yellow needles, which melt at 201°; it is only partially hydrolysed when heated with concentrated hydrochloric acid at 100—150°, and is very stable towards concentrated potash, but is readily hydrolysed when heated for a short time with hydriodic acid (b. p. 127°). The synthetical alizarin thus obtained melted at 260°, whereas pure alizarin melts at 289°. The low melting point is probably due to a small quantity of the methyl ether contained in the specimen.

J. J. S.

**Finland Turpentine.** By OSSIAN ASCHAN and EDVARD HJELT (*Chem. Zeit.*, 1894, **18**, 1566—1567).—Three samples of turpentine were examined: 1. Turpentine from South Finland. This was prepared from fir roots (*Pinus Abies*); after repeated distillation, the following fractions were obtained: 155—160° = 7.1; 160—165° = 30.2; 165—170° = 22.6; 170—175° = 20.1 per cent. The lowest fraction contained pinene. The others were redistilled, the portion boiling at 170—174° contained sylvestrene and dipentene, the remainder (b. p. 174—178°) contained dipentene but no sylvestrene. This turpentine is therefore similar in composition to Swedish and Russian. 2. Turpentine from North Finland. Prepared partly from wood tar and partly from pine wood, the fractions 160—165° and 165—170° were small, 170—174° = 32.2; 174—178° = 21.5 per cent., the former contained pinene, the latter dipentene and probably sylvestrene. 3. Turpentine prepared by the distillation of resinous wood with steam. The chief fraction, = 50 per cent., boiled at 155—156° and contained much pinene, the higher boiling portions contained sylvestrene but no dipentene, proving that the former compound is

contained in the wood, and that the latter is formed, during the distillation, from pinene. When treated with nitric acid, the lower fractions containing pinene yield, chiefly, terebic acid, whilst the higher fractions containing dipentene give terephthalic acid. The various terpenes were isolated and identified by the preparation of their hydrochlorides and nitroso-derivatives.

J. B. T.

**Limonene Nitrosochloride.** By OTTO WALLACH (*Ber.*, 1895, **28**, 1474).—The results of the determination of the molecular weights of the two nitrosochlorides quoted in a previous paper (this vol., i, 478) are falsified by an error in the calculation. In phenol solution, both the  $\alpha$ - and  $\beta$ -nitrosochloride have the bimolecular formula, so that the  $\beta$ -compound has the same molecular weight in solution in phenol and in benzene.

A. H.

**Compounds of the Carvacrol and Thymol Series.** By OTTO WALLACH and FRANZ NEUMANN (*Ber.*, 1895, **28**, 1660—1665).—Carvacrylamine may be obtained by the action of potash on isocarvoxime as well as on carvoxime (*Abstr.*, 1894, i, 536); the isocarvoxime employed was prepared by the elimination of hydrogen bromide from hydrobromocarvoxime, the latter being found by the authors, in agreement with Goldschmidt (*Abstr.*, 1887, 903), to melt at  $116^{\circ}$ , whereas Bacyer (*Abstr.*, 1894, i, 298) gives the melting point as  $136^{\circ}$ ; it is probable that two different hydrobromocarvoximes are formed under the varying conditions of the reaction.

*Amidocarcvacrol*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OH}$ , is formed by the reduction of nitrosocarcvacrol with tin and hydrochloric acid, the nitroso-derivative being prepared by the action of sodium ethoxide and amyl nitrite on carvacrol. The amido-compound is isolated in the usual manner as the *hydrochloride*; the latter forms thick prisms melting at  $214\text{--}215^{\circ}$ , and, on careful treatment with ammonia, yields the free base as a readily oxidisable precipitate, which separates from methylic alcohol in colourless crystals melting at  $134^{\circ}$ , and, on oxidation, yields thymoquinone. When boiled with acetic anhydride and anhydrous sodium acetate, it yields *triacetylamidocarcvacrol*,  $\text{C}_{10}\text{H}_{12}(\text{NAC}_2)\text{OAc}$ , which, after crystallisation from light petroleum, melts at  $75.5^{\circ}$ , and, on boiling with the requisite amount of aqueous soda, yields *acetylamidocarcvacrol*,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OH}$ , a crystalline compound melting at  $176\text{--}177^{\circ}$ . On methylation, it is converted into the *methylic ether*,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OMe}$ , crystallising in slender needles and melting at  $140^{\circ}$ ; when boiled with hydrochloric acid, the latter loses the acetyl group, forming the hydrochloride of *amidocarcvacrol methyl ether*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OMe}$ , which crystallises in needles melting at  $229^{\circ}$ , readily oxidises, and with ferric chloride gives a blue coloration. On acetylation, it forms the *diacetyl derivative*,  $\text{C}_{10}\text{H}_{12}(\text{NAC}_2)\cdot\text{OMe}$ , which crystallises in slender needles and melts at  $104^{\circ}$ .

*Amidothymol*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OH}$ , is obtained by the reduction of nitrosothymol, and is identical in all respects with the substance obtained by the action of sulphuric acid on carvoxime. Its *hydrochloride* begins to turn brown at  $240^{\circ}$ , and melts at  $255^{\circ}$ . Like amidocarcvacrol, it yields a *triacetyl* derivative, which crystallises in



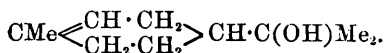
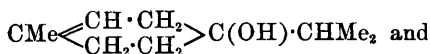
plates and melts at  $91^{\circ}$ . The *monacetyl* compound melts at  $174.5^{\circ}$ , and its *methylic ether* at  $139^{\circ}$ ; the *hydrochloride* of *amidothymol methyl ether*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_{12}\cdot\text{OMe}\cdot\text{HCl}$ , obtained by boiling the latter with hydrochloric acid, crystallises in long needles, melts at  $250^{\circ}$  with decomposition, and gives a blue colour with ferric chloride solution.

The only bromocarvacrol hitherto described is a liquid (Mazzara, *Gazzetta*, **16**, 194), but a crystalline preparation may be obtained by acting on carvacrol with bromine in acetic acid solution; it melts at  $46^{\circ}$  and boils at  $162\text{--}163^{\circ}$  under 12 mm. pressure. It yields an oily *acetyl* derivative and *methylic ether*, the latter boiling at  $147\text{--}150^{\circ}$  under 15 mm. pressure.

H. G. C.

**Constitution of Terpeneol.** By OTTO WALLACH (*Ber.*, 1895, **28**, 1773—1777; compare following abstract).—The exact constitution of terpeneol, although of such great importance, in view of the close relationship of this compound with so many other compounds of the terpene series, has not yet been proved, the position of the ethylene linking and the hydroxyl being still uncertain. The author has recently shown (this vol., i, 59) that it may be converted by a series of reactions into carvone, in which the ethylene linking is in the  $\Delta 1$  position, but in these reactions the possibility of intramolecular change was not excluded. Further research has shown, however, that the same change may be effected by acting on terpeneol nitrosochloride with hydrochloric acid, which converts it into a *hydroxyoxime*,  $\text{OH}\cdot\text{C}_{10}\text{H}_{15}\cdot\text{NOH}$ , melting at  $134^{\circ}$ ; this compound, when boiled with dilute acids, loses water and hydroxylamine, yielding a mixture of carvacrol and inactive carvone. It is very improbable that intramolecular change would take place in these reactions, and it may therefore be concluded that in terpeneol the ethylene linking is in the  $\Delta 1$  position.

With regard to the position of the hydroxyl group, the author has already shown (*Abstr.*, 1894, i, 43) that, on oxidation, terpeneol yields two compounds having the composition  $\text{C}_{10}\text{H}_{20}\text{O}_3$  and  $\text{C}_{10}\text{H}_{16}\text{O}_3$ ; the former, under suitable conditions, loses 3 mols.  $\text{H}_2\text{O}$ , forming cymene, and must therefore be a trihydroxyhexahydrocymene, two of the hydroxy-groups being in the 1 : 2 position, whilst the third must occupy the same position as the hydroxyl group in terpeneol, which is usually assumed to be the 4-position. Against this supposition is the fact that terpeneol yields terpenylic acid on oxidation, which is not readily understood if it contains the group  $\text{:C(OH)}\cdot\text{CHMe}_2$ , but would readily follow if the hydroxyl were in the side chain giving the group  $\text{:CH}\cdot\text{C(OH)Me}_2$ . As terpeneol is a tertiary alcohol, no other position of the hydroxyl group is possible, and it therefore remains to distinguish between the formulæ



In order to do this, the second of the above oxidation products,

having the formula  $C_{10}H_{16}O_3$ , was examined, and found to be a ketone, as it yields an *oxime*, melting at  $76-77^\circ$ , and a *semicarbazone*, melting at  $200^\circ$ . It also contains a lactone group, and on treatment first with soda and then with silver solution, yields the silver salt of an acid,  $C_{10}H_{18}O_4$ . It yields, as previously stated, terpenylic acid and acetic acid on oxidation, and on treatment with bromine in alkaline solution yields the same acid, together with bromoform or carbon tetrabromide. Hence it must be derived from terpenylic acid by the displacement of carboxyl by the group  $CH_2 \cdot COMe$ . The most probable constitution

of terpenylic acid is  $\begin{array}{c} O-CMe_2 \\ | \\ CO \cdot CH_2 \end{array} > CH \cdot CH_2 \cdot COOH$  (compare *Annalen*, **259**, 322; Schryver, this Journ., 1893, 1327; Wolff, *Inaug. Diss.*, Strasburg, 1894), and in that case the constitution of the above keto-

lactone must be  $\begin{array}{c} O-CMe_2 \\ | \\ CO \cdot CH_2 \end{array} > CH \cdot CH_2 \cdot CH_2 \cdot COMe$ , and the hydroxyl group in terpineol must be in the side chain, as shown by the second of the two formulæ given above. It is, however, possible, by assuming a number of intermediate reactions, to explain the conversion of terpineol into the ketolactone on the assumption of the first formula, and the former cannot therefore be yet regarded as absolutely disproved, although it is the less probable. If the new formula proves to be correct, many of the conclusions as to the orientation of compounds in the terpene series will have to be modified. H. G. C.

**Methoethylheptanonolide.** By FERDINAND TIEMANN and F. W. SEMMLER (*Ber.*, 1895, **28**, 1778—1781).—By the oxidation of pinene, the authors obtained, together with pinonic acid, a substance having the formula  $C_{10}H_{16}O_3$  (this vol., i, 477).—This compound is not, however, formed from pinene, but from an impurity contained in commercial pinene; it forms crystals melting at  $63-64^\circ$ , and is identical with the compound  $C_{10}H_{16}O_3$ , obtained by Wallach (see previous abstract) by the oxidation of terpineol. The authors have determined its constitution in almost the same manner as Wallach, and have arrived independently at the same constitutional formula, according to which it is *methyl-3'-ethyl-3-heptanon-6-olide-1-3'*. Like Wallach, they regard this as showing that in terpineol the hydroxyl group is in the side chain. H. G. C.

**Oxidation of Terpin, Terpin Hydrate, and Terpineol.** By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1895, **28**, 1781—1784).—Solid terpineol may be readily and quantitatively converted into terpin hydrate by mixing it with a little benzene and shaking the whole with 100 parts of 5 per cent. sulphuric acid for about five days. Liquid terpineol is also converted into terpin hydrate in the same manner, but 8—10 days are required for its complete conversion, and sufficient cineol is formed to be detected by its odour.

Terpin is converted by chromic anhydride, in acetic acid solution and in absence of water, into an orange compound, which explodes at  $150^\circ$ , and when warmed in acetic acid solution yields, together with re-formed terpin hydrate, the methoethylheptanonolide described in

the previous abstract. Terpin hydrate is not acted on by potassium permanganate at the ordinary temperature, but, on warming, it is completely resolved into simple compounds, such as acetic acid, oxalic acid, &c. From this behaviour it is probable that terpin hydrate is an open chain compound, the addition of the elements of water to terpin, which is usually represented as a dihydroxyhexahydrocymene, causing the opening of the closed chain at a point not yet determined.

The examination of the products of oxidation of solid terpineol has led to results in full agreement with those obtained by Wallach (see preceding abstracts). Liquid terpineol gives, in general, the same products on oxidation as the solid compound, although slight differences have been observed. Whether these differences are due to the fact that the two compounds are stereoisomeric, or whether the liquid terpineol contains small quantities of a structurally isomeric impurity, has not yet been determined.

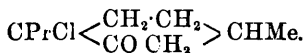
H. G. C.

**Some Derivatives of Menthol and of Menthene.** By IVAN KONDAKOFF (*Ber.*, 1895, **28**, 1618—1621).—Arth's conclusion (*Abstr.*, 1886, 892) is confirmed, that the menthylic chloride obtained by the action of phosphoric chloride on menthol is identical with the menthene hydrochloride obtained by the direct addition of hydrogen chloride to menthene. Further, menthylic bromide and menthene hydrobromide were each prepared in two ways, and the products in all four cases were identical; they boiled at 100—103° under 13 mm. pressure, and had a sp. gr. = 1.174—1.186 at 0° = 1.155—1.166 at 23°. This identity is contrary to what is to be expected, if we assume the correctness of the commonly accepted formula for menthene, and of the laws usually supposed to govern the addition of halogen acids to unsaturated compounds.

C. F. B.

**Orientation in the Terpene Series. Constitution of Carone.** By ADOLPH BAEYER (*Ber.*, 1895, **28**, 1586—1603; compare *Abstr.*, this vol., i, 379).—In order to obtain an insight into the nature of the products formed by the action of hydrogen chloride on bisnitroscarone, which are caronebisnitrosylic acid and a chlorinated ketone, the same reaction has been applied to the derivatives of menthone and tetrahydrocarvone. Bisnitrosomenthone (*Abstr.*, 1894, i, 522) reacts with alcoholic hydrogen chloride in the same way as bisnitroscarone, and, if the products be rapidly removed, *menthonebisnitrosylic acid* may be obtained as a crystalline mass, whilst the *monochloromenthone* is an oil. If the products are left too long in contact with the alcoholic hydrogen chloride, decomposition occurs, and menthone is formed.

Since the nitroso-group always enters the molecule in the  $\alpha$ -position relatively to the ketone group, and in this case is combined with a tertiary carbon atom, it follows from the constitution of menthone that the monochloromenthone formed has the formula

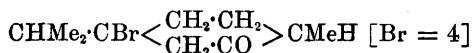


It is not identical with hydrochloropulegone, and on distillation with sodium acetate and acetic acid gives an unsaturated ketone, apparently identical with that prepared by Kremers (Abstr., 1894, i, 468) from menthene nitrosochloride.

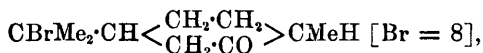
Bisnitrosotetrahydrocarvone yields *tetrahydrocarvonebisnitrosylic acid*, whilst *monochlorotetrahydrocarvone*,  $\text{CPrH} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{CMeCl}$ , yields an unsaturated ketone, which is not identical with carvotanacetone, since the *semicarbazide compound* melts at  $224^\circ$ , whilst that of carvotanacetone melts at  $177\text{--}179^\circ$ . This substance will be further described.

Carone combines with hydrogen bromide to form the hydrobromide of dihydrocarvone, and it is therefore important to know the constitution of the latter. Dihydrocarveol hydrobromide, when treated with silver acetate, yields an oil, which on hydrolysis is converted into a *glycol*,  $\text{C}_{10}\text{H}_{18}(\text{OH})_2$ ; this crystallises in slender, white needles, melting at  $110\cdot5\text{--}112^\circ$ . This glycol is attacked by hydrobromic acid in the cold, forming a heavy oil, and therefore contains a tertiary hydroxyl group. Hence the bromine atom which has been displaced by hydroxyl must have been combined with a tertiary carbon atom, since the hydroxyl group of dihydrocarveol is a secondary one. The glycol is converted by oxidation into a ketone, the *semicarbazide compound* of which crystallises in large prisms, and melts at  $139^\circ$ .

Dihydrocarvone hydrobromide, when treated with silver acetate, yields an oil, which by hydrolysis and treatment with sodium and alcohol is converted into the glycol just described. The bromine atom of dihydrocarvone hydrobromide must therefore have the position 4 or 8, and, although it has hitherto been found impossible to definitely settle the question, it appears most probable that it has the position 4. A hydrobromodihydrocarvone of the formula



can yield three dihydrocarvones, whilst if the formula be



only one dihydrocarvone can result.

When *i*-hydrobromodihydrocarvone is distilled with sodium acetate and acetic acid, a mixture of two ketones, dihydrocarvone and carvenone, is formed, a reaction which clearly shows the close relation between these two substances. When the hydrobromide is treated with silver acetate, an oil is formed, which is coloured blue by sodium nitrite and hydrochloric acid, and is probably the third ketone. It is, however, very unstable, and decomposes when distilled.

The fact that alcoholic substances containing the 4:8 double linking form blue nitrosochlorides, whilst dihydrocarveol does not, seems to show that the latter, and therefore also dihydrocarvone, does not contain a 4:8 double linking, so that the double linking of dihydrocarvone must be in the ring, and the bromine atom can only enter the position 4. Dihydrocarveol and its derivatives yield hydrobromides

which can be converted into very unstable substances, which probably do contain the 4:8 double linking, and form blue nitrosochlorides, an additional proof that this linking is absent from dihydrocarveol itself.

1-Bisnitroso-4-bromotetrahydrocarvone, prepared from 1-dihydrocarvone, crystallises in rhombic tablets which melt and decompose at 131°. The corresponding derivative of *i*-dihydrocarvone melts at 140°. The corresponding chloro-derivative of *i*-dihydrocarvone forms small needles, and melts at 142°; this last substance is decomposed by alcoholic hydrogen chloride, with formation of *i*-dichlorodihydrocarvone, which crystallises in almost rectangular tablets melting at 66—68°. This compound is identical with the substance formed by the action of alcoholic hydrogen chloride on bisnitrosocarone, prepared from *i*-carvone. *i*-Dibromodihydrocarvone is formed by the action of alcoholic hydrogen chloride on *i*-bisnitrosobromotetrahydrocarvone, and is identical with the product obtained in a similar manner from the bisnitrosocarone prepared from *i*-carvone. The same compound has also been obtained by Wallach from dihydrocarvone by the action of hydrobromic acid and bromine.

*a*-Dichlorodihydrocarvone crystallises in colourless needles melting at 42°. *a*-Dibromodihydrocarvone, which crystallises in tablets melting at 96—97°, is formed from bisnitrosocarone, and has also been prepared by Wallach from dihydrocarvone. The various modes of formation of these compounds show that the halogen atoms in them must have the position 1:4.

Since the bisnitroso-compound of 4-chlorotetrahydrocarvone is converted by hydrogen chloride into the same 1:4-dichlorotetrahydrocarvone as is obtained from bisnitrosocarone, it follows that the nitroso-group of the latter, and therefore the hydrogen atom in carone, must occupy position 1. The formula for carone is therefore

most probably  $\text{CPr} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{CH} \end{array}$ , since any other possible arrangement would involve the presence of a trimethylene ring.

The presence of a methylene group adjacent to a keto-group may be proved in compounds of the terpene series by converting them into a hydroxymethylene compound by the action of an ethereal formate, decomposing this with dilute alkali, and showing that the substance regained is identical with the original ketone. Treated in this way, carone undergoes reduction to tetrahydrocarvone, which is therefore regained instead of the original carone. The semicarbazide compound of *a*-tetrahydrocarvone crystallises in prisms melting at 194—196°.

The substance previously (this vol., i, 380) described as carone-bisnitrosone proved to be simply impure bisnitrosocarone.

A. H.

**Essence of Cananga.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1895, [3], 13, 140—142; compare this vol., i, 425).—The essence, after hydrolysis with potash and distillation with steam, yielded an oil boiling at 170—210°, and this, when reduced with sodium, was resolved into a volatile oil and an alkylic oxide. The alcohol from the

latter possessed the properties of linalool,  $C_{10}H_{18}O$ ; it boiled at  $193-200^\circ$ ; its sp. gr. =  $0.8751$  at  $15.5^\circ$ , and the refractive index is  $1.46920$  at the same temperature, whence the molecular refraction =  $48.86^\circ$ . Part of the *volatile oil* boiled at  $171-175^\circ$ , and approximated in composition to that required by the formula  $C_9H_{12}O$ ; sp. gr. =  $0.9325$ ; refractive index =  $1.49702$ . It was probably either paramethoxytoluene or paramethoxyethylbenzene, as it yielded anisic acid on oxidation. JN. W.

**Camphoric Acid.** By WILLIAM A. NOYES (*Amer. Chem. J.*, 1895, 17, 421—434).—This paper consists of a detailed account of the investigation summarised in this vol., i, 295.

The depression of the freezing point of acetic acid by cis-campholytic acid establishes the molecular formula  $C_8H_{13}COOH$  for the acid, and Walker has privately informed the author that the ethylic salt of "camphothetic acid" has the molecular weight 182; hence the identity of the two acids is proved. A. G. B.

**The Products of Oxidation of Camphoric acid.** By LUIGI BALBIANO (*Ber.*, 1895, 28, 1506—1508; compare *Abstr.*, 1894, i, 614).—The bibasic acid,  $C_8H_{14}O_4$ , obtained by the reduction of the acid,  $C_8H_{12}O_5$ , is converted by oxidation into asymmetric dimethylsuccinic acid, and is probably  $\alpha\beta\beta$ -trimethylglutaric acid,



since it cannot be converted into the known dimethylsuccinic acid, melting at  $139^\circ$ , and when heated with acetic chloride, yields an anhydride which crystallises in interpenetrating plates, and melts at  $80-81^\circ$ .

The acid,  $C_8H_{12}O_4$ , which accompanies the one just mentioned, is a monobasic lactonic acid, and forms a *silver salt*,  $C_8H_{11}O_4Ag$ , and a crystalline *barium salt*,  $(C_8H_{11}O_4)_2Ba \cdot 4H_2O$ . When heated with alkalis, the corresponding hydroxy-acid is formed, the *silver salt* of which,  $C_8H_{12}O_5Ag_2$ , is a white crystalline precipitate. On heating the lactonic acid with sulphuric acid, carbonic anhydride is evolved, but the acid formed has not yet been obtained in quantity sufficient for examination. A. H.

**Campholenic acid and Campholenamides.** By AUGUSTE BÉHAL (*Compt. rend.*, 1895, 120, 927—930).—The campholenamide melting at  $86-87^\circ$  is obtained by heating camphoroxime at  $100^\circ$  with twice its weight of hydrogen chloride in aqueous solution, and heating the nitrile with alcoholic potash.

The amide melting at  $130.5^\circ$  is obtained from the nitrile formed by the action of slightly more than the calculated quantity of acetic chloride or thionyl chloride on camphoroxime. It crystallises from alcohol of  $60^\circ$  in prismatic needles, and is probably identical with the amide already known and described as melting at  $124-127^\circ$ .

The amide melting at  $106^\circ$  is obtained from the nitrile which is formed, if, after the action of the acetic chloride on the oxime has ceased, the product is heated at  $100^\circ$  for about 10 minutes. If the

heating is more prolonged, the resulting nitrile yields the amide melting at  $92^{\circ}$ .

The amide which melts at  $106^{\circ}$  forms large lamellæ and its melting point is not altered by repeated crystallisation from water or toluene. On hydrolysis, it yields two campholenic acids, one of which melts at  $50^{\circ}$ , whilst the other is a liquid boiling at  $152^{\circ}$  under a pressure of 13 mm. If, however, the amide is repeatedly crystallised from twice its weight of alcohol of  $60^{\circ}$ , it splits up into the amides melting at  $130.5^{\circ}$  and  $86^{\circ}$  respectively and hence seems to be a molecular combination of the two. In a similar manner the amide that melts at  $92^{\circ}$  can be split up into those melting at  $130^{\circ}$  and  $86^{\circ}$ .

It would seem, therefore, that there are really only two campholenamides, one melting at  $130.5^{\circ}$ , and the other at  $86^{\circ}$ . The former is converted into the latter by heating with hydrochloric acid in presence of dilute alcohol.

In presence of benzene, the amide melting at  $130.5^{\circ}$ , combines with 2 mols. of hydrogen iodide (owing to the presence of an ethylenic as well as an amido-group), and if the product is treated at once with an alkali the original amide is regenerated, but if it is allowed to remain exposed to the air for not less than 48 hours, and is then heated with an alkali, it yields the amide melting at  $86^{\circ}$ , together with campholenolide, which boils at  $258^{\circ}$  under a pressure of 760 mm., and exists in both a gelatinoid and a well-crystallised form, which melt at the same temperature,  $30^{\circ}$ .

When the liquid campholenic acid is converted into the ethylic salt by the action of hydrogen chloride in presence of alcohol, the solid acid is obtained on hydrolysis, but if the ethylic salt is formed by the action of ethylic iodide on the sodium salt, it regenerates the liquid acid when hydrolysed.

The ammonium salt of the solid acid, when heated at  $280^{\circ}$ , yields the amide melting at  $86^{\circ}$ , whereas the liquid acid as Goldschmidt and Zurrer have shown, yields the amide melting at  $130.5^{\circ}$ .

The liquid acid and its nitrile and amide are optically active, whereas the solid acid and its derivatives are not, and hence it would seem that the solid acid is a racemic form of the liquid. Attempts to resolve the former into two optically active forms by crystallisation of the strychnine and cinchonine salts were unsuccessful, and if the action of moulds also gives negative results it will follow that the isomerism of the liquid and solid campholenic acids is analogous to that of fumaric and maleic acids (compare this vol., i, 241).

C. H. B.

**New Glucoside allied to Amygdalin.** By EMIL FISCHER (*Ber.*, 1895, 28, 1508—1513).—Amygdalin is regarded by H. Schiff (*Annalen*, 1870, 154, 337) as a derivative of benzaldehyde cyanhydrin with a disaccharide. The nature of this disaccharide is unknown; the author believes, however, that amygdalin is a derivative of maltose or of a similarly constituted diglucose, and for the following reasons. When amygdalin is submitted to the action of yeast extract, in presence of toluene, at  $35^{\circ}$  for seven days, half the sugar residue is split off as glucose (compare this vol., i, 7), without

the nitrogenous portion of the molecule being attacked. Under these conditions there is obtained a glucoside—*benzalnitride glucoside*,  $\text{CN}\cdot\text{CHPh}(\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5)$ , which closely resembles amygdalin. It crystallises from hot chloroform, of which it requires 2000 parts for dissolution, in colourless needles, sinters together at  $140^\circ$ , and melts at  $147\text{--}149^\circ$ . Its specific rotatory power at  $20^\circ$  ( $c. = 8\text{--}9$ ) is  $[\alpha]_D = -26.7^\circ$ ; the bitter taste is more pronounced than that of amygdalin. Boiled with alkali, ammonia is evolved, and a product formed which is probably analogous to amygdalinic acid. The new glucoside yields glucose when warmed with 5 per cent. hydrochloric acid, and when treated with emulsin, glucose, benzaldehyde, and hydrogen cyanide are formed. Since amygdalin is tolerably disseminated in the vegetable kingdom, the new glucoside may also occur in nature; and it may, perhaps, be found possible to isolate it from the apparently impure preparation described as “amorphous amygdalin” or “laurocerasin” (Lehmann, *Neues Rep. f. Pharm.*, **23**, 449).

A. R. L.

**Quercetin Derivatives.** By JOSEF HERZIG (*Monatsh.*, 1895, **16**, 312—320; compare Abstr., 1888, 1309; 1890, 64; 1891, 1386; 1893, i, 413).—The author reviews his previous work on quercetin derivatives and on the constitution of quercetin, and in opposition to Liebermann (this vol., i, 429), still maintains that it is represented by the formula  $\text{C}_{15}\text{H}_{10}\text{O}_7$ . He further shows that *dibromacetyl-tetraethylquercetin*,  $\text{C}_{25}\text{H}_{26}\text{Br}_2\text{O}_8$ , can be prepared by the interaction of dibromotetraethylquercetin (1 part) and acetic anhydride (10 parts), in presence of zinc chloride (1 part). It dissolves readily in alcohol, crystallises in pale yellow needles, and melts at  $154\text{--}157^\circ$ . Dibromoethyleuxanthone,  $\text{C}_{15}\text{H}_{10}\text{Br}_2\text{O}_4$ , which crystallises in yellow needles, and melts at  $205\text{--}207^\circ$ , readily yields a *monacetyl* derivative,  $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}_5$ . This crystallises in yellow needles or scales, melts at  $186\text{--}190^\circ$ , and, on hydrolysis, readily forms the original dibromoethyleuxanthone.

G. T. M.

**Phenylcoumalin and “Dicotoïn.”** By GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1895, **28**, 1549—1558).—Dicotoïn has been shown to be a compound of phenylcoumalin with cotoïn. Phenylcoumalin has the power of combining with many phenols to form crystalline compounds, which, however, become dissociated in solution. *Phenylcoumalin-catechol* forms large, light yellow crystals, melting at  $64\text{--}66^\circ$ . *Phenylcoumalin-resorcinol* melts at  $110^\circ$ , and *phenylcoumalin-quinol* at  $108^\circ$ . The resorcinol and catechol compounds crystallise in the monosymmetric system, whilst the quinol compound is asymmetric.

When phenylcoumalin is fused with potash, it yields, among other products, *paradiphenylcarboxylic acid*, which melts at  $224^\circ$ , although the melting point has been previously stated as  $218\text{--}219^\circ$ . It is not impossible that the *hydroxyphenylcoumalinic acid*, obtained by Hesse by fusing *hydroxyphenylcoumalin* with potash, may contain a certain amount of this substance. *Hydroxyphenylcoumalin* is, according to Hesse, a constituent of the *pseudodicotoïn* which accompanies cotoïn in Coto bark. The authors have carefully examined



the bark, but have been unable to obtain any other substances from it than cotoïn, paracotoïn, and phenylcoumalin. They draw attention to the fact that hydroxyphenylcoumalin and phenylcoumalin possess very similar properties. A. H.

**Alantolactone (Helenin).** By JULIUS BREDT and WILHELM POSTH (*Annalen*, 1895, 285, 349—384).—Helenin is the crystalline substance obtained from the root of *Inula Helenium*. Many years ago it was investigated by Gerhardt, Kallen, and others, but the uncertainty of the views regarding its nature has led the authors to submit it to examination, and as its properties are in close agreement with those of the lactone of an unsaturated hydroxy-acid, they propose to call it alantolactone.

*Alantolactone*,  $C_{15}H_{20}O_2$ , is obtained on distilling commercial helenin at  $192^\circ$  under a pressure of 10 mm.; it crystallises from alcohol in white needles, and melts at  $76^\circ$ . It is volatile in an atmosphere of steam, and is scarcely soluble in hot water, being readily soluble in organic solvents; the lactone is insoluble in a cold solution of sodium carbonate, which dissolves it when warmed, forming the sodium salt of alantolic acid.

*Alantolic acid*,  $OH \cdot C_{14}H_{20} \cdot COOH$ , is prepared by adding, to an ice-cold solution of the sodium salt, hydrochloric acid in amount insufficient to decompose the whole quantity, in order to avoid formation of the lactone; it melts at  $94^\circ$  (compare Kallen, *Ber.*, 1876, 9, 155). The *barium* salt crystallises in stellar aggregates, and the crystals which separate from water contain  $5H_2O$ ; the *calcium* salt contains  $6H_2O$ . The *methylic* salt is very soluble in organic solvents, and melts at  $83^\circ$ ; the *ethylic* salt melts at  $79-80^\circ$ . When an aqueous solution of the sodium salt is boiled, separation of the lactone takes place, and this also occurs when a current of carbonic anhydride is led into a boiling solution of the barium salt; on adding a few drops of a dilute, mineral acid to a hot aqueous solution of alantolic acid, immediate separation of the lactone takes place. The amide is obtained from the lactone or from ethylic alantolate by dissolving it in alcoholic ammonia; it melts and decomposes at  $197^\circ$ , and has been already described by Kallen. The *acetyl* derivative of the amide crystallises in needles, and melts with decomposition at  $179^\circ$ . Alantolactone is regenerated when methylic alantolate is heated at  $170-180^\circ$ , methylic alcohol being eliminated; the amide also yields the lactone when heated at  $200^\circ$ , liberation of ammonia taking place.

Alantolactone is an unsaturated compound containing two ethylenic linkings, and the following additive compounds have been prepared. The *monhydrochloride* crystallises in long needles, and melts at  $117^\circ$ , elimination of hydrogen chloride occurring at  $150^\circ$ ; the *dihydrochloride* crystallises in needles and leaflets, melts and decomposes at  $127-134^\circ$ , and yields the monhydrochloride when treated with boiling alcohol. The *monhydrobromide* crystallises from alcohol, and melts at  $106^\circ$ ; the *dihydrobromide* melts at  $117^\circ$ , hydrogen bromide being eliminated.

*Hydroalantolactone*,  $C_{15}H_{22}O_2$ , is obtained by suspending alantolactone in cold water, and allowing it to remain in contact with

sodium amalgam for eight or ten days, and it may be prepared from the mono- and di-hydrochloride also, in the same way; it melts at  $123^{\circ}$ , and boils at  $195^{\circ}$  under a pressure of 13 mm. The *hydrochloride* is formed by the action of hydrogen chloride on hydroalantolactone suspended in absolute alcohol; it melts and decomposes at  $120^{\circ}$ .

The salts of *hydroalantolic acid*,  $\text{OH} \cdot \text{C}_{11}\text{H}_{22} \cdot \text{COOH}$ , are obtained on dissolving the lactone in alkalis. The *barium* salt is anhydrous, and dissolves readily in water, the aqueous solution becoming decomposed at  $100\text{--}105^{\circ}$ , or when submitted to the action of carbonic anhydride. The *silver* salt is somewhat soluble in water, and decomposes after long exposure to light. The *amide* crystallises from alcohol, and melts at  $186^{\circ}$ , ammonia being liberated.

When alantolactone is heated with phosphoric anhydride at  $100^{\circ}$  to  $120^{\circ}$ , liberation of carbonic oxide takes place, and the *hydrocarbons*  $\text{C}_{12}\text{H}_{16}$  and  $\text{C}_{13}\text{H}_{16}$  are formed; both substances are liquid, yield naphthalene when heated, and under a pressure of 10 mm. boil at  $132^{\circ}$  and  $152^{\circ}$  respectively, whilst the latter boils at  $288^{\circ}$  under atmospheric pressure. Distillation of alantolactone from zinc dust gives rise to naphthalene, propylene, and two liquid *hydrocarbons*,  $\text{C}_{11}\text{H}_{16}$  and  $\text{C}_{12}\text{H}_{16}$ , which boil, under a pressure of 10 mm., at  $93\text{--}94^{\circ}$  and  $122^{\circ}$  respectively, whilst the latter, under atmospheric pressure, boils at  $266^{\circ}$ , a portion becoming decomposed.

M. O. F.

**Phycocerythrin.** By H. MOLISCH (*Chem. Centr.*, 1895, i, 159; from *Apoth. Zeit.*, 1894, 920—921).—Red six-sided prisms of this colouring matter can be observed in the cells of the dead twigs of the alga *Nitophyllum punctatum*. The phycocerythrin dissolves on submerging the alga in water for 24 hours in the dark, and may be precipitated by alcohol. By repeated solution in water and precipitation by alcohol, a pure aqueous solution may be obtained, which yields crystalloids of the colouring matter on spontaneous evaporation; it is insoluble in alcohol, ether, or carbon bisulphide, and is turned green by concentrated potash. It gives the albumin reactions, and is therefore classed as a proteid. It is bleached by light or dilute potash, and decomposes at  $64^{\circ}$ ; it seems to be identical with the rhodospermin of the various *Bornetia* and *Ceramia*, and with the red colouring matter of the *Nemastoma* and *Wrangelia*.

W. J. P.

**Beet Pectin.** By K. ANDRIK (*Chem. Centr.*, 1895, i, 28; from *Böhm. Zeit. Zuck. Ind.*, 1894, 19, 101—113).—The pectin extracted from sliced beet may be precipitated by alcohol; the precipitated pectin contains calcium sulphate which cannot be completely removed, and when fresh is soluble in water, but after drying until its weight becomes constant, it is only partly soluble. The extent to which pectin is precipitated from its solution by alkalis, lime, or magnesia, is dependent on the temperature, but complete precipitation is never effected by these reagents; after precipitating a solution of fresh pectin with lead acetate, the filtered solution is not appreciably active, although the original solutions are dextrorotatory.

W. J. P.

**Platosodiammoniodipyridine Compounds.** By PETER KLASON (*Ber.*, 1895, **28**, 1489—1492); compare this vol., ii, 400).—According to Jörgensen (*J. pr. Chem.*, 1886, [2], **33**, 501), the same product is obtained by treating ammonioplatochloramine chloride with pyridine, or pyridineplatochloropyridine chloride with ammonia. In the same way, the product obtained by treating ammonioplatinous chloride with pyridine is identical with that formed from pyridineplatinous chloride and ammonia, and on treatment with acids yields both ammonioplatinous chloride and pyridineplatinous chloride. This has been explained by Jörgensen by means of structural formulæ, and by Werner on the ground of geometrical isomerism (*Zeit. anorg. Chem.*, **3**, 267). The author finds, however, that when ammonioplatinous chloride is treated with pyridine at a low temperature ( $5^{\circ}$ ), a salt which he terms *ammonioplatinosopyridine chloride*,  $(\text{NH}_3)_2\text{Pt}(\text{C}_5\text{H}_5\text{NCl})_2 + \text{H}_2\text{O}$ , is produced, which has the same composition, but is quite distinct from that obtained by Jörgensen. The latter, which is termed *pyridineplatinosammonium chloride*,  $(\text{C}_5\text{H}_5\text{N})_2\text{Pt}(\text{NH}_4\text{Cl})_2 + \text{H}_2\text{O}$ , is obtained when pyridineplatinous chloride is treated with ammonia even at a low temperature. The two salts may be distinguished by their solubility in water, in which the new compound is much more readily soluble than the isomeride, and by their behaviour towards potassium chloroplatinite, chloroplatinic acid, potassium iodide, &c. The new isomeride is completely converted into that previously obtained when it is heated at  $100^{\circ}$ , or incompletely when its solution in water is boiled. The inverse change appears to take place to some extent when the old salt is heated with acids, as both ammonioplatinous chloride and pyridineplatinous chloride are formed.

The existence of these two isomeric substances shows that the theory of Werner (*Zeit. anorg. Chem.*, **3**, 267), according to which the two should be identical, must receive some modification.

A. H.

**Synthesis of Pyridine Derivatives from Coumalin Compounds.** By MAX GUTHZEIT (*Annalen*, 1895, **285**, 36--60; compare *Abstr.*, 1894, i, 71).—The action of organic bases on ethylic 6-ethoxycoumalin-3:5-dicarboxylate has been investigated as a sequel to the study of the behaviour of this substance towards dry ammonia (*loc. cit.*). The present paper embodies interesting theoretical considerations with the results of the investigation, which are described in the two following abstracts.

M. O. F.

**Action of Ethylamine on Ethylic 6-Ethoxycoumalin-3:5-dicarboxylate.** By EMIL HAUSSMANN (*Annalen*, 1895, **285**, 61—107).—*Ethylic 6:1:2:3:5-Ethoxyethylketocarboxy dihydropyridine-carboxylate*,  $\text{CH} \begin{smallmatrix} \text{C}(\text{COOEt}) : \text{C}(\text{OEt}) \\ \text{C}(\text{COOH}) \end{smallmatrix} \text{----CO} > \text{NEt}$ , is obtained by vigorously agitating finely powdered ethylic ethoxycoumalindicarboxylate with an aqueous, 2 per cent. solution of ethylamine for ten minutes; it crystallises in colourless needles and melts at  $81^{\circ}$ . The compound dissolves with difficulty in light petroleum, but is readily soluble in other organic solvents, and is slightly soluble in hot water, forming an

acid solution. When it is heated at  $170^{\circ}$ , carbonic anhydride is eliminated, but the quantity set free indicates that a certain amount of the substance loses water at this temperature, forming a stable anhydride. Metallic salts yield a precipitate with a neutral solution of the ammonium salt; the *silver* salt is anhydrous. On heating the compound with fuming hydrochloric acid for six hours at  $130$ – $140^{\circ}$ , and subsequently at  $180^{\circ}$ , carbonic anhydride, ethylic chloride, ethylamine hydrochloride are formed. The *diethylic* salt is obtained by the action of ethylic iodide on the silver salt; it crystallises from light petroleum in small, colourless needles, and melts at  $56^{\circ}$ . The *ethylamine* additive-compound,  $C_{13}H_{17}O_6N + 2NH_2Et$ , is formed on adding an ethereal 10 per cent. solution of ethylamine to the ethylic salt (m. p.  $81^{\circ}$ ) dissolved in a small quantity of benzene; it is a white, crystalline powder which sinters at  $110^{\circ}$ , and melts at  $158$ – $160^{\circ}$ , but when it is suddenly heated to  $130^{\circ}$  fusion takes place and gas is evolved, the substance solidifying and finally melting at  $160^{\circ}$ . The additive compound is decomposed by warm water, ethylamine being eliminated, and on treating the liquid with an acid, separation of the ethylic salt takes place.

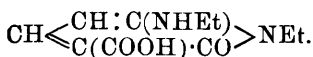
6 : 1-*Hydroxyethyl-2-pyridone*,  $CH \begin{smallmatrix} \text{CH:C(OH)} \\ \text{CH} \text{---} \text{CO} \end{smallmatrix} > NEt$ , is obtained by heating the ethylic salt (m. p.  $81^{\circ}$ ) with an 11 per cent. solution of potassium hydroxide for three hours on the water-bath; it is a colourless substance which sublimes when heated, and melts at  $141^{\circ}$ . The aqueous solution colours the skin intense violet, and on adding potassium dichromate to a dilute, acid solution, a deep blue coloration is developed, a green flocculent precipitate being formed when hydrogen peroxide is employed; the latter reagent gives rise to a blue coloration if the solution is alkaline. Silver nitrate and mercuric chloride are reduced by the aqueous solution; a red coloration is developed in the alcoholic solution by ferric chloride, but it gives a reddish-brown precipitate in aqueous solutions. The *hydrochloride* crystallises in brownish leaflets, and decomposes on treatment with water.

*Ethylic* 6 : 1 : 2 : 3 : 5-*hydroxyethylketocarboxy dihydropyridinecarboxylate*,  $CH \begin{smallmatrix} \text{C(COOEt):C(OH)} \\ \text{C(COOH)} \text{---} \text{CO} \end{smallmatrix} > NEt$ , is obtained by heating the ethoxy-compound (m. p.  $81^{\circ}$ ) with concentrated sulphuric acid at  $100^{\circ}$  for  $2\frac{1}{2}$  hours; it separates from dilute alcohol in small, colourless crystals and melts at  $103^{\circ}$ . The compound is also formed when a 5 per cent. solution of alcoholic potash is employed as a hydrolytic agent. Carbonic anhydride is eliminated on heating the substance at  $150^{\circ}$ , and the residue when dissolved in alcohol develops a deep reddish-violet coloration with ferric chloride, this effect being also produced by the original substance. Solutions of metallic salts, with the exception of mercuric nitrate and silver nitrate, yield a precipitate with a neutral solution of the ammonium salt.

*Ethylic* 6 : 1 : 2 : 3 : 5-*ethylamidoethylketocarboxy dihydropyridinecarboxylate*,  $CH \begin{smallmatrix} \text{C(COOEt):C(NHEt)} \\ \text{C(COOH)} \text{---} \text{CO} \end{smallmatrix} > NEt$ , is formed when the action of an aqueous solution of ethylamine on ethylic ethoxycoumal-

indicarboxylate is allowed to continue during 24 hours; it crystallises in small, colourless needles, and melts at  $165^{\circ}$ , carbonic anhydride being eliminated above this temperature. The compound is also obtained from the ethylamine additive compound of ethylic ethoxyethylketocarboxy dihydropyridinecarboxylate by boiling the solution in benzene. The *ethylamine* salt,  $C_{13}H_{18}O_5N_2 \cdot NH_2Et$ , is prepared by treating the latter compound with an ethereal 10 per cent. solution of ethylamine.

6 : 1 : 2 : 3 : 5-*Ethylaminoethylketodihydropyridinedicarboxylic acid*,  $CH \leq \begin{matrix} C(COOH) : C(NHEt) \\ C(COOH) \end{matrix} \text{---} CO > NEt$ , is prepared by allowing ethylic ethoxycoumalindicarboxylate to remain in contact with an aqueous solution of ethylamine for three weeks; it crystallises from alcohol in small leaflets, and if suddenly heated at  $180^{\circ}$  melts at  $191^{\circ}$  with evolution of carbonic anhydride. It dissolves in alkalis and alkali carbonates; the alcoholic solution develops a deep-red coloration with ferric chloride. The substance is also formed when the foregoing ethylic salt is hydrolysed with a boiling, aqueous solution of potash (6 per cent.), a small quantity of hydroxyethylpyridine being formed at the same time; the latter compound is not produced, however, when hydrolysis is allowed to proceed at the ordinary temperature during 24 hours. If the ethylic salt (m.p.  $165^{\circ}$ ) is heated with concentrated sulphuric acid for three hours on the water-bath, carbonic anhydride is eliminated and ethylic alcohol is formed, the constitution of the resulting *compound* being represented by one of the formulæ,  $CH \leq \begin{matrix} C(COOH) : C(NHEt) \\ CH \end{matrix} \text{---} CO > NEt$ , and



It crystallises from alcohol in colourless leaflets and melts at  $207^{\circ}$ , after being suddenly heated to  $200^{\circ}$ , carbonic anhydride being evolved at the higher temperature; an alcoholic solution of the acid gives a deep-red coloration with ferric chloride.

Whilst the foregoing compounds are produced by the action of aqueous ethylamine on ethylic ethoxycoumalindicarboxylate, different results are obtained when water is excluded from the reaction.

*Ethylic* 1 : 2 : 6 : 3 : 5-*ethyldiketotetrahydropyridinedicarboxylate*,  $CH \leq \begin{matrix} CH(COOEt) \cdot CO \\ C(COOEt) \end{matrix} \cdot CO > NEt$ , is prepared by adding an ethereal  $2\frac{1}{2}$  per cent. solution of ethylamine (1 mol.) to ethylic ethoxycoumalindicarboxylate dissolved in the minimum quantity of benzene; it crystallises in colourless needles and melts at  $123^{\circ}$ . The substance is neutral and the alcoholic solution does not develop colour with ferric chloride. When heated on the water bath with aqueous potash, it yields hydroxyethylpyridone, whilst the action of cold alkali gives rise to a *compound* which melts at  $132^{\circ}$ . The *ethylamine* additive-compound is a yellow oil having the composition  $C_{13}H_{17}O_6N + 2NH_2Et$ .

*Ethylic* 6 : 1 : 2 : 3 : 5-*hydroxyethylketodihydropyridinedicarboxylate*,

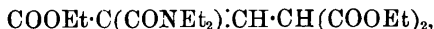
$\text{CH} \begin{smallmatrix} \text{C}(\text{COOEt})\text{:C}(\text{OH}) \\ \text{C}(\text{COOEt})\text{---CO} \end{smallmatrix} > \text{NEt}$ , is isomeric with the foregoing compound, and is obtained by heating it to its melting point; it is also formed when a warm ethereal solution of ethylamine acts on ethylic ethoxycoumalindicarboxylate. The substance crystallises from light petroleum in colourless needles and melts at  $89.5^\circ$ ; it develops an intense red coloration with ferric chloride, forms salts with alkalis, and does not yield carbonic anhydride under the influence of heat. The *ethylamine* salt is a yellow powder which dissolves readily in water and melts at  $181^\circ$ ; the aqueous solution, on treatment with silver nitrate, yields the *silver* salt,  $\text{C}_{13}\text{H}_{16}\text{O}_6\text{NAg}$ , which is not changed by light. The ethyl ether obtained by the action of ethylic iodide on the silver salt melts at  $56^\circ$ ; it is identical with the ethyl ether prepared from ethylic ethoxyethylketocarboxy dihydropyridinecarboxylate.

When ethylamine and ethylic ethoxycoumalindicarboxylate dissolved in benzene remain together for several days, diethylmalonamide,  $\text{CH}_2(\text{CONHET})_2$ , is formed (compare Ruhemann and Morrell, *Trans.*, 1891, 43).

The action of dilute aqueous diethylamine on ethylic ethoxycoumalindicarboxylate gives rise to a *compound*,



it is a basic oil which does not yield a definite hydrochloride. If water is excluded from the reaction, the *compound*,



is formed; it is a yellow oil which yields diethylamine when treated with boiling soda.

Aqueous triethylamine is without action on ethylic ethoxycoumalindicarboxylate.

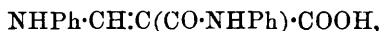
M. O. F.

**Action of Aniline on Ethylic 6-Ethoxycoumalin-3:5-dicarboxylate and on Ethylic Dicarboxyglutaconate.** By GEORG BAND (*Annalen*, 1895, 285, 108—153).—*Ethylic* 1:2:6:3:5-*phenyldiketotetrahydropyridinedicarboxylate*,  $\text{CH} \begin{smallmatrix} \text{CH}(\text{COOEt})\cdot\text{CO} \\ \text{C}(\text{COOEt})\text{---CO} \end{smallmatrix} > \text{NPh}$ , is prepared by dissolving finely powdered ethylic ethoxycoumalindicarboxylate (10 grams) in a solution of aniline (10 grams) in ether (50 c.c.); it crystallises in pale yellow leaflets, and melts at  $147^\circ$ , becoming solid above this temperature, and melting finally at  $197^\circ$ . The substance dissolves sparingly in ether, alcohol, and light petroleum; it is insoluble in cold water, and is decomposed by boiling water, this effect being also produced by a hot solution of sodium carbonate. The alcoholic solution does not give any coloration with ferric chloride; aniline converts the substance into a compound which crystallises in colourless needles, and melts at  $117^\circ$  (see below).

*Ethylic* 6:1:2:3:5-*hydroxyphenylketodihydropyridinedicarboxylate*,  $\text{CH} \begin{smallmatrix} \text{C}(\text{COOEt})\text{:C}(\text{OH}) \\ \text{C}(\text{COOEt})\text{---CO} \end{smallmatrix} > \text{NPh}$ , is isomeric with the foregoing compound, and is obtained by heating it at the melting point or by

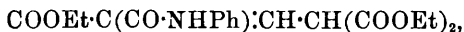
treating it with boiling alcohol; the change is also effected by allowing the substance to remain in contact with cold alcohol. It crystallises in slender, white needles, and melts at  $197^{\circ}$ ; it is more soluble in alcohol than the isomeride, and forms a *sodium* salt on treatment with sodium carbonate. The *silver* salt separates on adding silver nitrate to a solution of the sodium salt; it can also be obtained from the *potassium* salt in the same manner. The *ethylic* salt is prepared by the action of ethylic iodide on the silver salt; it crystallises in silky needles and melts at  $115^{\circ}$ . Ferric chloride produces a deep reddish-violet coloration in the alcoholic solution of the substance, this reaction distinguishing it from the isomeride; the action of aniline also is different, in the cold, there is no action, but boiling aniline converts it into the *dianilide*,  $\text{CH} \begin{smallmatrix} \diagup \text{C}(\text{CO}\cdot\text{NHPH})\text{:C}(\text{OH}) \\ \diagdown \text{C}(\text{CO}\cdot\text{NHPH})\text{---CO} \end{smallmatrix} \text{>NPh}$ ; this crystallises from dilute alcohol and melts at  $265^{\circ}$ .

Reference has already been made to the formation of a compound melting at  $117^{\circ}$  on treating ethylic phenyldiketotetrahydropyridinedicarboxylate (m. p.  $147^{\circ}$ ) with aniline. This substance is the monanilide of ethylic anilidoethylenedicarboxylate obtained by Ruhemann and Morrell on treating ethylic amidoethylenedicarboxylate with aniline (this vol., i, 20); in preparing it from ethylic dicarboxylglutaconate by the action of aniline, a certain amount of malondianilide is formed, which is also produced on heating the coumalin derivative with aniline. Hydrolysis with alcoholic soda converts it into the *monanilide* of *anilidoethylenedicarboxylic acid*,



which crystallises in colourless leaflets, and melts and evolves gas at  $182.5^{\circ}$ .

The *monanilide* of ethylic dicarboxylglutaconate,



is obtained by adding a solution of aniline in ether to ethylic ethoxycoumalindicarboxylate dissolved in the minimum quantity of benzene, it is a yellow oil, which does not solidify when cooled. This substance is also formed by the action of aniline on ethylic dicarboxylglutaconate, when heated on the water bath, it is converted into ethylic hydroxyphenylketodihydropyridinedicarboxylate (m. p.  $197^{\circ}$ ).

Ethylic diketotetrahydropyridinedicarboxylate, melting at  $178\text{--}179^{\circ}$  (Guthzeit, Abstr., 1894, i, 72), is converted by aniline into the monanilide of ethylic anilidoethylenedicarboxylate (m. p.  $117^{\circ}$ ) malondianilide and the monamide of ethylic malonate being formed at the same time; the same compounds are produced when aniline acts on ethylic ethyldiketotetrahydropyridinedicarboxylate, which melts at  $123^{\circ}$  (Hanssmann, preceding abstract).

An aqueous solution of aniline has the same effect on ethylic ethoxycoumalindicarboxylate as the anhydrous base, converting it into ethylic phenyldiketotetrahydropyridinedicarboxylate (m. p.  $147^{\circ}$ ), and this compound is also formed when a dilute aqueous solution of aniline acetate is employed.

M. O. F.

**Substituted Amido-derivatives of Aldehydecollidine.** By PETER KNUDSEN (*Ber.*, 1895, **28**, 1759—1761).—The aldehydecollidine obtained by the interaction of aldehydeammonia and paraldehyde contains, in addition to methylethylpyridine, small quantities of trimethylpyridine, as already shown by Auerbach (*Abstr.*, 1893, **i**, 175), who separated the two bases by means of the different solubilities of their mercurochlorides in water. A more convenient method is to convert them into the picrates and to separate these by fractional crystallisation from water, in which trimethylpyridine picrate is readily soluble.

The author has already shown that bromine acts on aldehydecollidine with formation of the substitution product, bromethyl- $\alpha$ -picoline,  $C_5NH_5Me \cdot CHMeBr$ . The bromine atom may be readily displaced by hydroxyl (*Abstr.*, 1893, **i**, 43), and a similar reaction occurs with primary amido-bases, substituted amido-derivatives of aldehydecollidine being formed. Methylamine converts it into *methylamidocollidine*,  $C_6NH_5 \cdot CHMe \cdot NHMe$ , which is a colourless liquid, having a penetrating, pyridine-like odour; it is soluble in water, and boils at 223—225°. Its physiological properties strongly resemble those of nicotine. The *hydrochloride*,  $C_6N_2H_{14} \cdot 2HCl$ , crystallises in slender needles and melts at 177°, and the *platinochloride*,



in flat prisms melting at 243°, whilst the *nitroso-compound* is an inodorous oil. *Anilidocollidine*,  $C_6NH_5 \cdot CHMe \cdot NHPh$ , is obtained by the action of aniline on bromethyl- $\alpha$ -picoline, and crystallises in reddish-coloured prisms melting at 145—146° (uncorr.); the *hydrochloride* crystallises in slender needles melting at 201—202°, the *platinochloride*,  $C_{14}N_2H_{16} \cdot H_2PtCl_6$ , in prisms which carbonise above 300°, and the *acetyl* compound in snow-white rods melting at 100°.

Attempts were also made to displace the bromine atom in bromethyl- $\alpha$ -picoline by cyanogen, but without success. In presence of water, picolylmethylalkine is formed, and in its absence tarry, brominated condensation products are formed, from which no nitrile could be isolated.

H. G. C.

### Conversion of Aliphatic Oximes into Pyridine Derivatives.

By MAX SCHOLTZ (*Ber.*, 1895, **28**, 1726—1733).—*Cinnamylideneacetone hydroxime*,  $CHPh \cdot CH \cdot CH \cdot CH \cdot CMe \cdot NOH$ , crystallises in small, pale yellow needles, melting at 153°. The *acetyl derivative* forms lustrous plates and melts at 83°. The oxime is not converted into a pyridine derivative by the action of dehydrating agents, but, when distilled at high temperatures, 2:6-methylphenylpyridine is obtained; this is a colourless liquid, which quickly turns yellow, volatilises with steam, and boils at 280—281° (corr.). The yield is 25 per cent. of the oxime employed. The *platinochloride*,  $(C_{12}H_{11}N)_2 \cdot H_2PtCl_6 + H_2O$ , crystallises in red needles, and, when dry, melts and decomposes at 200°. The *aurochloride* is deposited in large, golden-yellow needles, melting at 150—151°. The *mercurochloride* crystallises in silky, lustrous, the *picrate* in yellow, needles, and melts at 135°. With chromic acid, the



base yields a dicarboxylic acid, which melts at the same temperature as dipicolinic acid.

When oxidised with the calculated quantity of potassium permanganate, 6:2-phenylpyridinecarboxylic acid is formed; it crystallises in large, silky, lustrous needles, melts at  $109^{\circ}$ , and under boiling water, and gives a red coloration with ferrous sulphate; when heated to  $190$ – $200^{\circ}$ , carbonic anhydride is evolved, and 6-phenylpyridine is formed; this was identified by means of the picrate and platinochloride, and its production proves the constitution of the acid and of the methylphenylpyridine. The silver salt of the acid crystallises in small stellate needles; the hydrochloride is also crystalline.

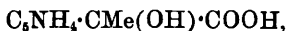
2:6-Methylphenylpiperidine, prepared by the reduction of the pyridine with sodium and alcohol, is a colourless liquid, which boils at  $257$ – $259^{\circ}$  (corr.). The hydrochloride crystallises in colourless needles, the aurochloride in sparingly soluble, golden plates, melting at  $97^{\circ}$ . The platinochloride, picrate, and benzoyl derivative are oily.

Cinnamylideneacetophenone,  $\text{CHPh:CH:CH:COPh}$ , prepared from cinnamaldehyde and acetophenone, crystallises in long, golden needles, melting at  $102$ – $103^{\circ}$ , and gives a cherry-red coloration with concentrated sulphuric acid. The oxime crystallises in almost colourless needles, and melts at  $131^{\circ}$ . When strongly heated, the oxime yields 2:6-diphenylpyridine, which crystallises in colourless needles, melts at  $81^{\circ}$ , boils at  $396$ – $398^{\circ}$  (corr.), yields benzoic acid when oxidised with chromic acid, and is completely decomposed by potassium permanganate. The yield is about 30 per cent. of the oxime employed. This base appears to be identical with the 2:6-diphenylpyridine prepared by Doebner and Kuntze by the oxidation of  $\alpha$ -phenyl- $\alpha$ -naphthacinchonic acid, but the platinochloride and methiodide differ from those which Paal and Strassner obtained from the diphenylpyridine formed from diphenylacetic acid and ammonia; the latter compound is therefore probably not the 2:6-derivative as they state. The platinochloride crystallises with  $2\text{H}_2\text{O}$  in long, orange needles, melting at  $195^{\circ}$ . The aurochloride is deposited in large, yellow needles and melts at  $204^{\circ}$ . The picrate crystallises in dark yellow needles, the methiodide in almost colourless prisms, melting at  $169^{\circ}$  and  $194^{\circ}$  respectively.

2:6-Diphenylpiperidine, formed by the reduction of the pyridine, boils at  $367$ – $368^{\circ}$  (corr.), and becomes viscid when cooled. The hydrochloride is crystalline and melts at  $298^{\circ}$ . The platinochloride and aurochloride could not be prepared; the picrate melts at  $198^{\circ}$ . Cinnamylideneacetone oxime and cinnamylideneacetophenone oxime; in addition to pyridine derivatives, might also yield compounds containing only 5 atoms in the ring; the former appears to do this, as the lower fraction obtained during the distillation gave the pyrroline reaction, but the substance was only formed in very small quantity.

J. B. T.

**Derivatives of Picoline- $\alpha$ -lactic acid.** By PETER KNUDSEN (*Ber.*, 1895, 28, 1762–1773).—A 3-pyridine- $\alpha$ -lactic acid,



has been obtained by Hardy and Calmels (*Abstr.*, 1886, 724, 815,

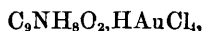
900, 1048; 1837, 1057) by the hydrolysis of pilocarpine, but hitherto it has not been obtained synthetically. The homologous picoline- $\alpha$ -lactic acid has been obtained by the author from the 6-picoly-3-methylalkine formed by the action of water on bromethyl-methylpyridine (Abstr., 1893, i, 43). The former substance melts at 36—37°, boils at 252—253° (uncorr.), and is converted by treatment with chromic acid in acetic acid solution into the corresponding *picolyl methyl ketone*,  $C_8NH_3Me \cdot COMe$ ; this boils at 232—233°, and forms a *platinochloride*,  $(C_8NH_3O)_2H_2PtCl_6$ , which crystallises in small plates, and melts and decomposes at 195°. It readily combines with hydrogen cyanide at the ordinary temperature, yielding the *cyanhydrin*,  $C_8NH_3Me \cdot CMe(OH) \cdot CN$ , which crystallises from benzene in slender needles, melts at 103—104°, and is insoluble in water; this is quantitatively converted, on hydrolysis, into *picoline- $\alpha$ -lactic acid*,  $C_8NH_3Me \cdot C(OH) \cdot COOH$ , which can be purified by conversion into the barium salt. The acid crystallises from chloroform, on the addition of benzene, in lustrous plates melting at 158—159° (uncorr.). It is very readily soluble in water and alcohol, and when not quite pure can only be obtained as an amorphous, gummy mass. The metallic salts are all amorphous; the *hydrochloride*,  $C_8NH_{11}O_3 \cdot HCl$ , crystallises in large prisms or plates melting at 190—191°; the *hydrobromide*,



in large prisms melting at 219—220°; the *platinochloride* in small prisms very soluble in water and alcohol; and the *aurochloride*,  $C_8NH_{11}O_3 \cdot HAuCl_4$ , in felted needles melting at 114°. When treated with phosphorus tribromide in carbon bisulphide solution, it is converted into *picoline- $\alpha$ -bromopropionic acid*,  $C_8NH_3Me \cdot CMeBr \cdot COOH$ , which is a very unstable syrup, but yields an *aurobromide*,



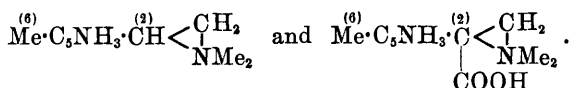
crystallising in well developed, dark violet plates, and melting at 156—157°. The salts of the acid very readily pass into the corresponding *picolineacrylic acid*,  $C_8NH_3Me \cdot C(:CH_2) \cdot COOH$ , with separation of a metallic bromide; for its preparation, the barium salt is best employed, the resulting barium salt being decomposed with the requisite quantity of sulphuric acid. It is thus obtained as a brownish syrup with a strongly acid reaction, whose *aurochloride*,



crystallises in small rods melting at 167—168°.

Hardy and Calmels succeeded in synthesising pilocarpine by heating pyridine- $\alpha$ -lactic acid with trimethylamine in a sealed tube; but in view of the readiness with which the picolyl-lactic acid loses hydrogen bromide, a synthesis of a homologue of pilocarpine is unlikely to be effected in this manner, and, in fact, the products of the action are trimethylamine hydrobromide and picolineacrylic acid. At the ordinary temperature, the action proceeds differently, two basic compounds being obtained, one of which can be distilled over in a current of steam, and is a strongly odorous basic oil, soluble in water, and yields with gold chloride the salt  $C_{11}N_2H_{18} \cdot 2AuCl_3$  melt-

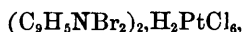
ing at 136—138°; it may also be isolated from the mixture of bases by treating them with baryta water and extracting with ether, the non-volatile portion remaining as a barium salt. The ethereal solution on evaporation yields the base in a pure condition, and if it is then dissolved in hydrochloric acid and gold chloride added, the normal *aurochloride*,  $C_{11}N_2H_{16}, 2HAuCl_4$ , separates in plates melting at 159—160°. The non-volatile substance readily loses carbonic anhydride forming the volatile base, and yields an *aurochloride*,  $C_{12}N_2H_{18}O_2(AuCl_3)$ , which melts at 141—143° and decomposes at 195—200° with evolution of carbonic anhydride. The constitution of these two compounds is probably represented by the following formulæ:—



Dimethylamine acts on picoline- $\alpha$ -bromopropionic acid in a similar manner, forming a volatile base,  $C_{10}N_2H_{16}$ , which is probably *dimethylamidocollidine*,  $C_5\text{MeNH}_3\cdot\text{CMe}\cdot\text{NMe}_2$ .

The difference between the behaviour of the author's picoline- $\alpha$ -bromopropionic acid and Hardy and Calmels' pyridine- $\alpha$ -bromopropionic acid makes it somewhat doubtful whether the two acids are strictly homologous, and the author suggests that possibly Hardy and Calmels' acid is in reality pyridine- $\beta$ -bromopropionic acid. H. G. C.

**1 : 3-Dibromoquinoline.** By ADOLPH CLAUS and ARNALDO CARSELLI (*J. pr. Chem.*, 1895, [2], 51, 477—490; compare Abstr., 1890, 172).—This dibromoquinoline melts at 101°. The *hydrochloride*,  $C_9H_5NBr_2\cdot HCl$ , crystallises in thick, colourless laminæ, and melts at 202°; water and alcohol dissociate it. The *platinochloride*,



forms yellow needles and decomposes at 289°.

4 : 1 : 3-Nitrodibromoquinoline melts at 159° (not 162°, *loc. cit.*), and the corresponding *amido*-derivative at 178—180°. The latter yields a *methiodide* which crystallises in yellow needles and melts at 238°; this fact is of interest as indicating that the entrance of an amido-group into the 4-position confers upon 1 : 3-dibromoquinoline the capacity to combine with methylic iodide, whilst the entrance of this group into the ortho-position hinders such combination; no methiodide has been obtained from 1 : 2 : 4-amidodibromoquinoline. The *hydrochloride* and *platinochloride* of 4 : 1 : 3-amidodibromoquinoline are described; the *zincchloride* decomposes and melts at 325—330°.

1 : 3 : 4-Tribromoquinoline is prepared from 4 : 1 : 3-amidodibromoquinoline through the diazo-reaction; it crystallises in colourless, lustrous needles and melts at 159°. Its *hydrochloride* and *platinochloride* are described.

1 : 3 : 3'-Tribromoquinoline has been misnamed 1 : 4 : 4'- and 1 : 3 : 4'-tribromoquinoline (Abstr., 1890, 1321; 1891, 82); the latter of these two orientations now stands corrected by the recent observation of Claus and Howitz (Abstr., 1894, i, 617), that 3'-, not 4'-, derivatives

are the products of the Claus-Collischonn method for preparing haloïd quinolines (Abstr., 1887, 60). It melts at  $169.5^{\circ}$ . This tribromoquinoline is formed when a boiling solution of 1 : 3-dibromoquinoline is brominated with the theoretical proportion of bromine, and this is the sole instance in which bromine can easily be introduced into the 3'-position of a quinoline already substituted in the benzene-ring, without recourse to the Claus-Collischonn method. The best yield of this tribromoquinoline is obtained by brominating 1-quinolinesulphonic acid.

The products of the nitration of 1 : 3 : 3'-tribromoquinoline have already been described (Abstr., 1890, 1321); it is now noted that the supposed nitro-derivative melting at  $195^{\circ}$  (*loc. cit.*) is not an individual compound, but a mixture of 4 : 1 : 3 : 3'-nitrotribromoquinoline (m. p.  $215^{\circ}$ ) with unchanged tribromoquinoline. When 4 : 1 : 3 : 3'-nitrotribromoquinoline is heated with sulphuric acid, and the liquid thus obtained is diluted and made alkaline with ammonia, a compound which appears to be *hexabromodiquinolyl*,  $C_{18}H_6Br_6N_2$ , is precipitated; this crystallises in colourless needles and melts at  $239^{\circ}$ ; hot glacial acetic acid and hot chloroform dissolve it, but it is insoluble in alkalis and in hydrochloric acid.

1 : 3 : 4 : 3'-*Tetrabromoquinoline*, previously misnamed 1 : 3 : 4 : 4'-(Abstr., 1894, i, 473), can be sublimed in the form of small, colourless needles; it melts at  $205^{\circ}$ , and is sparingly soluble in hydrochloric acid and in hot alcohol.

A. G. B.

**1 : 4-Dibromoquinoline.** By ADOLPH CLAUS and F. WOLF (*J. pr. Chem.*, 1895, [2], 51, 490—397).—The nitro-1 : 4-dibromoquinoline previously described (Abstr., 1890, 172), is now shown to be the 3-nitro-derivative. The corresponding amido-derivative melts at  $162^{\circ}$ , not  $165^{\circ}$  (*loc. cit.*); no methiodide could be obtained from it; its *platinochloride* is described.

1 : 4 : 3'-*Tribromoquinoline* has been misnamed 1 : 4 : 4'-tribromoquinoline (Abstr., 1891, 83); like the 1 : 3 : 3'-derivative, it yields a diquinolyl-condensation product of high melting point ( $236^{\circ}$ ) as well as 3 : 1 : 4 : 3'-nitrotribromoquinoline, when it is nitrated (compare preceding abstract).

A. G. B.

**1 : 3-Dimethylquinophthalone and 1 : 3-Dimethylquinaldinic acid.** By GEORG PANAJOTOW (*Ber.*, 1895, 28, 1511—1513).—1 : 3-

*Dimethylquinophthalone*,  $C_8NH_4Me_2CH \leq \begin{matrix} O \cdot CO \\ | \quad | \\ C \quad C_6H_4 \end{matrix}$  [CH = 2'; CO : C = 1 : 2], is prepared by heating dimethylquinaldine with phthalic anhydride and zinc chloride at  $140$ — $150^{\circ}$ ; after purification, it crystallises from glacial acetic acid in yellow needles, melts at  $282^{\circ}$ , and is insoluble in water and alcohol. The yield is equal to the quinaldine employed. The *sulphonic acid*,  $C_{20}H_{14}O_2N \cdot SO_3H$ , is brownish-yellow and amorphous; it dissolves in water, and dyes silk and wool, directly, of a golden yellow colour. The *nitro-derivative*,  $C_{20}H_{14}O_2N \cdot NO_2$ , is colourless, flocculent, and amorphous. *Dimethylquinaldinic acid*,  $C_8NH_4Me_2 \cdot COOH$  [Me : Me : COOH = 1 : 3 : 2'], obtained when the

phthalone is oxidised by chromic acid, crystallises from alcohol in yellow needles, and gives an amorphous platinochloride. The yield is small. J. B. T.

**Anthrapyridine.** By A. PHILIPS (*Ber.*, 1895, **28**, 1658—1660).—The anthrapyridines corresponding with the  $\alpha$ - and  $\beta$ -anthrapyridine-quinones described by the author (*Abstr.*, 1894, i, 554), may be obtained from these by warming them with zinc dust and dilute aqueous ammonia.  $\beta$ -Anthrapyridine,  $C_{13}H_9N$ , is usually obtained in amorphous flocks, but on sublimation forms yellow, nacreous plates, the greater portion of the substance being, however, carbonised. It is sparingly soluble in water, readily in the other common solvents, the solutions having a blue or bluish-green fluorescence, whilst the salts are yellow, and give greenish-yellow solutions with a green fluorescence. The hydrochloride crystallises in small, yellow needles, and the platinochloride in microscopic prisms.  $\alpha$ -Anthrapyridine is also usually obtained in amorphous flakes, but sublimes in reddish-yellow needles, a large amount of carbonisation also taking place; it melts at  $275^\circ$ , and is less soluble than the  $\beta$ -compound. The solutions of the salts only show a slight fluorescence. H. G. C.

**Synthesis of Dihydroglyoxalines.** By GEORGE C. CLAYTON (*Ber.*, 1895, **28**, 1665—1669).—The readiness with which allylbenzamide undergoes condensation with formation of an oxazoline (Kay, *Abstr.*, 1894, i, 77) has led the author to examine the behaviour of the acidyl allylamines towards aromatic amido-compounds; the results show that dihydroglyoxalines may be readily obtained in this manner.

*Allylacetamide*,  $CH_2:CH\cdot CH_2\cdot NHAc$ , obtained by heating allylthiocarbimide with acetic acid for 36 hours, under slightly increased pressure, after rectification boils at  $215^\circ$ , and has a sp. gr. = 0.9608 at  $15^\circ$ ; it combines with hydrogen chloride to form a hygroscopic hydrochloride.

*Allylformamide*,  $CH_2:CH\cdot CH_2\cdot NH\cdot COH$ , is obtained in a similar manner from allylthiocarbimide and formic acid, and boils at  $109^\circ$  under 15 mm. pressure; its sp. gr. = 1.0078 at  $0^\circ$ .

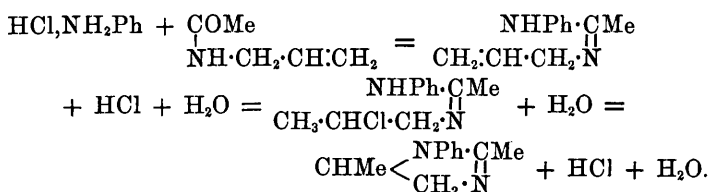
2 : 5 : 4-Dimethylphenyldihydroglyoxaline,  $CHMe < \begin{smallmatrix} NPh\cdot CMe \\ CH_2\cdot N \end{smallmatrix}$ , is obtained by heating allylacetamide and aniline hydrochloride at  $180^\circ$  for 10 hours; the product is treated with dilute hydrochloric acid, which leaves acetamide undissolved, the solution being shaken with ether to remove the last traces of this substance, made alkaline, and again extracted with ether. The dihydroglyoxaline is a colourless oil, which has an ethereal, and at the same time a quinoline-like odour, and yields a hygroscopic hydrochloride.

2 : 5 : 4-Dimethylparatolyldihydroglyoxaline, obtained in a similar manner from allylacetamide and paratoluidine hydrochloride, is an oily base, which boils at  $145^\circ$  under 15 mm. pressure.

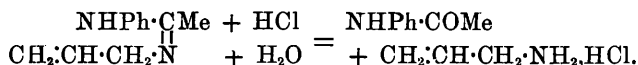
2 : 5 : 4-Methyldiphenyldihydroglyoxaline, prepared from aniline hydrochloride and allyl benzamide, is crystalline, melts at  $65^\circ$ , and boils at  $192^\circ$  under 12 mm. pressure. These three bases may also be

obtained by heating allylamine hydrochloride with acetanilide, aceto-paratoluidide, and benzamide respectively.

The mechanism of the action in the formation of the dihydro-glyoxalines is explained by the author in the following manner.



The formation of acetanilide and allylamine is explained by the hydrolysis of the first intermediate compound by the water liberated in the reaction.

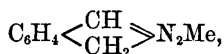


The reaction is therefore incomplete and reversible, as shown by the fact already mentioned, that the same bases may be obtained by heating allylamine with the acidylamides. H. G. C.

**Action of Chloroform and Alcoholic Potash on Diamines: New Synthesis of Benzoylglyoxaline.** By G. GRASSI-CRISTALDI and G. LAMBARDI (*Gazzetta*, 1895, 25, i, 224—230).—A mixture of chloroform and alcoholic potash readily acts on orthophenylenediamine hydrochloride with development of heat; the characteristic odour of an isonitrile is at first apparent, but disappears on keeping the mixture at 50° for an hour. The alcohol and chloroform are now distilled off under reduced pressure, and the product distilled in a current of steam; by extracting the residue with ether, benzoylglyoxaline, melting at 170°, is obtained. Hofmann's reaction thus seems to proceed with orthophenylenediamine in such a way as to yield an intermediate isonitrile of the constitution  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}$ , which then changes into the glyoxaline,  $\text{C}_6\text{H}_4 < \begin{array}{c} -\text{N} \\ \text{NH} \end{array} > \text{CH}$ .

No pure substance could be isolated on similarly treating meta-phenylenediamine, but on treating its para-isomeride with chloroform and alcoholic potash, a very small quantity of a crystalline substance was obtained; this melted at about 160°, and approximated in composition to that of a diisonitrile,  $\text{C}_6\text{H}_4(\text{N} \cdot \text{C})_2$ . W. J. P.

**Phthalazine.** By SIEGMUND GABRIEL and FRANZ MÜLLER (*Ber.*, 1895, 28, 1830—1835; compare *Abstr.*, 1893, i, 732).—Phthalazine is better prepared from 1 : 2-tetrabromo-xylene,  $\text{C}_6\text{H}_4(\text{CHBr}_2)_2$ , which is obtained by allowing the theoretical quantity of bromine to drop slowly into 1 : 2-xylene heated to 140°; it melts at 115—117°. It unites with methylic iodide, forming an additive product, which crystallises in pointed, yellow needles, and melts at 235—240°, and when digested with potash yields dihydromethylphthalazine,



and 3-methylphthalazone (Abstr., 1893, i, 346); if silver oxide is employed instead of potash, the phthalazone is alone obtained. Dihydromethylphthalazine is an oil with an odour suggestive of that of isoquinoline; it readily oxidises to the phthalazone; the white *hydrochloride* and yellow *picrate* form needles melting respectively at 140—141° and 93—95°. It yields a *methiodide*, which melts at 153—154°, and, when treated with alkalis, forms a base, the *hydrochloride* of which melts at 159—161°.

*Phthalazine ethiodide* can be prepared like the corresponding methyl compound; it forms yellow needles, melts at 204—210°, and yields a base, that readily oxidises to ethylphthalazone. The last substance can also be prepared from potassio-phthalazone and ethylic iodide; it melts at 55—58°, or 59—60°, according to the method of preparation. With benzylic chloride, phthalazine yields, moreover, a compound which melts at 97—99°, and with ethylic chloracetate a compound which melts at 155—159°, and forms a yellow picrate, melting at 129—131°.

C. F. B.

**Pyrazines and Piperazines.** By CARL STOEHR (*J. pr. Chem.*, 1895, [2], 51, 449—476; compare Abstr., 1893, i, 486).—Dimethylpyrazine is obtained in good yield by heating ammonium salts (a mixture of chloride and phosphate) with glycerol, which yields acraldehyde,  $2\text{NH}_3 + 2\text{C}_2\text{H}_3\cdot\text{COH} = \text{C}_6\text{H}_8\text{N}_2 + 2\text{H}_2\text{O} + \text{H}_2$ . By introducing acetic aldehyde, dimethylethylpyrazine is formed (compare Storch, Abstr., 1886, 1044). To prepare pyrazine, the dimethyl derivative may be oxidised to pyrazinedicarboxylic acid, which yields the base when heated in glacial acetic acid at 200°.

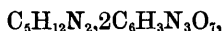
Pyrazine crystallises in colourless prisms, melts at 47°, and boils at 118° (768·4 mm.) (compare Wolff, Abstr., 1893, i, 373). Its vapour burns with a reddish flame, and an odour of hydrocyanic acid. It usually behaves as a monacid base, but is occasionally diacid. The following salts and derivatives have not yet been described. The *nitrate*,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{HNO}_3$ ; the *sulphate*,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{H}_2\text{SO}_4$  (m. p. 136—137°); the *zinc chloride* compound,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{ZnCl}_2$ ; the *mercuri-chloride*,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{HgCl}_2$  (crystallographical measurements given), decomposes and melts at 273°; the *copper sulphate* compound,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{CuSO}_4 + 5\text{H}_2\text{O}$ ; the *platinic chloride* compounds,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{H}_2\text{PtCl}_6$  and  $(\text{C}_4\text{H}_4\text{N}_2)_2\text{HCl}\cdot\text{PtCl}_4$ ; the *methiodide*,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{MeI}$ ; the *periodide*, which is a crystalline brownish-red precipitate, obtained by adding a solution of iodine in potassium iodide to one of pyrazine; and the *methochloride*,  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{MeCl}$ , together with its *platinum* salts,  $(\text{C}_4\text{H}_4\text{N}_2\cdot\text{MeCl})_2\cdot\text{PtCl}_4$ , and  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{MeCl}\cdot\text{PtCl}_4$ , its *mercuri-chloride*  $\text{C}_4\text{H}_4\text{N}_2\cdot\text{MeCl}\cdot 6\text{HgCl}_2$  (m. p. 217—218°), and its *gold* salt.

Methylpyrazine has been already described (Abstr., 1894, i, 384); it behaves as a monacid base, and the salts which it forms with mineral acids are more soluble than those of pyrazine. The *picrate*,  $\text{C}_6\text{H}_8\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallises in short prisms, melts at 133°, and dissolves very sparingly in cold water, but more freely in alcohol. The *mercuric chloride* compound,  $\text{C}_6\text{H}_8\text{N}_2\cdot 2\text{HgCl}_2$ , melts and decomposes

at 194—195°, and is very sparingly soluble in cold water. The *silver* compound crystallises in slender, colourless needles. The *aurochloride*,  $C_5H_6N_2 \cdot HAuCl_4$ , melts at 116—117°, and is stable only in hydrochloric acid solution, for when water is added, the *salt*,  $C_5H_6N_2 \cdot AuCl_3$ , separates; this melts at 145—146°. The *methiodide*,  $C_5H_6N_2 \cdot MeI$ , melts at 129—130°; the *methochloride* was crystallised, and its *platinic chloride* compound,  $(C_5H_6N_2 \cdot MeCl)_2 \cdot PtCl_4$ , *mercuric chloride* compound, and *gold salt* were prepared.

Pyrazinecarboxylic acid (Abstr., 1893, i, 487) crystallises in anhydrous, colourless prisms; its aqueous solution has a strong acid reaction, and gives a reddish-yellow coloration with ferrous sulphate. It melts and decomposes at 229—230°. The barium salt crystallises with  $3\frac{1}{2}H_2O$ ; the copper salt with  $2H_2O$ .

*Methylpiperazine*,  $C_5H_{12}N_2$ , is prepared by reducing methylpyrazine in alcoholic solution by means of sodium; the liquid is diluted with water, distilled, and the distillate evaporated with hydrochloric acid to obtain the hydrochloride, from which the base is liberated by an alkali. It crystallises in lustrous, white laminae, boils at 155—155.5° (at 763 mm.), and dissolves freely in water, alcohol, chloroform, and benzene, but less freely in ether. Its aqueous solution is alkaline, and it behaves as a diacid base. The *hydrochloride*,  $C_5H_{12}N_2 \cdot 2HCl$ , crystallises from hot alcohol in lustrous, colourless needles, melts at 248—249°, and dissolves in water, yielding an acid solution. The *platinochloride*,  $C_5H_{12}N_2 \cdot H_2PtCl_6$ , *mercurochloride*, and *picrate*,



are described. The *dinitrosamine*,  $C_5H_{10}N_2(NO)_2$ , prepared by treating the aqueous solution of the hydrochloride with sodium nitrite and hydrochloric acid, crystallises in brilliant, large, dendritic laminae, melts at 71°, and dissolves sparingly in water and ether, but more freely in alcohol.

Dibenzoylmethylpiperazine,  $C_5H_{10}N_2(COPh)_2$ , obtained by shaking the hydrochloride with benzoic chloride and caustic soda in aqueous solution, separates, when water is added to its solution in hot alcohol, in colourless, lustrous, well-formed tables, which are anhydrous, and melt at 147°. If the proportion of water added to the alcoholic solution be considerable, the crystals contain  $2H_2O$ . A. G. B.

**Constitution of *n*-Phenylpyrazolone.** By R. v. ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 522—525).—The appearance of a paper by Claisen and Haase (this vol., i, 193) elicits some further remarks from v. Rothenburg concerning the constitution of his 1-phenyl-5-pyrazolone (compare this vol., i, 303). Walker's "phenylmethyloxy-pyrazole" (Abstr., 1894, i, 476) was described in French and English patent specifications in 1893; since it is derived from diacetylphenylhydrazine by loss of water, its constitution is that of a 2:3-phenyl-methylpyrazolone. A. G. B.

**Pyrazolone Derivatives.** By R. HIMMELBAUER (*J. pr. Chem.*, 1895, [2], 51, 532).—In reference to Knorr's remarks on the phenol form of 1:3-phenylmethyl-5-pyrazolone (this vol., i, 396), the author points out that he has obtained an ethylic carboxylate of this pyrazo



lone by the action of ethylic chlorocarbonate on an alkaline aqueous solution of the pyrazolone. This melts at  $28^{\circ}$ , and is easily hydrolysed by aqueous ammonia, carbonic anhydride being eliminated and methylphenylpyrazolone produced; this fact, together with the absence of the iron reaction, shows that the carboxethyl is attached to oxygen. By heating monochloracetic acid with methylphenylpyrazolone in alkaline solution, Knorr's methylphenylpyrazolone-carboxylic acid (m. p.  $178^{\circ}$ ) is obtained.

A. G. B.

**Synthesis of Antipyrine.** By R. VON ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 572—574).—A reply to Stolz (this vol., i, 394).

A. G. B.

**Isomerism in the Pyrazole Series.** By R. VON ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 574—577).—A reply to Knorr (this vol., i, 395).

A. G. B.

**Chemical Equivalence.** By R. VON ROTHENBURG (*J. pr. Chem.*, 1895, [2], 51, 577—578).—In his recent papers (this vol., i, 395—398), Knorr obviously holds the opinion that the methyl and phenyl groups are chemically equivalent, and sets aside the accepted view that they differ in their influence on a compound. To direct attention to this is, in the author's opinion, sufficient to indicate the value of Knorr's criticisms.

A. G. B.

**Synthesis of Quinazolines.** By STEFAN V. NIEMENTOWSKI (*J. pr. Chem.*, 1895, [2], 51, 564—572).—Excellent yields of quinazoline derivatives are to be obtained by heating anthranilic acid or its homologues with amides of fatty acids, although the yield decreases as the molecular weight of the amide increases. Thus, 4'-hydroxyquinazoline is prepared by heating anthranilic acid (13 grams) with formamide (7—8 grams) in a flask for some three hours at  $120$ — $130^{\circ}$  and crystallising the product from alcohol; the author finds the melting point of this substance to be  $212^{\circ}$ . In a similar manner, 4':2-hydroxymethylquinazoline (m. p.  $238^{\circ}$ ) has been synthesised from metamidoparatoluic acid and formamide; 2':4'-methylhydroxyquinazoline from anthranilic acid and acetamide; and 4':2:2'-hydroxydimethylquinazoline (m. p.  $255^{\circ}$ ) from metamidoparatoluic acid and acetamide (see Abstr., 1889, 1065).

4':2'-Hydroxyethylquinazoline,  $C_8H_4 < \begin{matrix} N=CEt \\ C(OH):N \end{matrix}$ , from anthranilic

acid and propionamide, crystallises in slender, white needles, melts at  $225^{\circ}$ , and dissolves in water and most organic solvents, as well as in acids and alkalis. A little propionanilide is formed at the same time. In all cases where a temperature above  $140^{\circ}$  is requisite to effect these syntheses, the anthranilic acid or its homologues is partly decomposed, with production of an aromatic base, which reacts with the fatty amide, yielding the corresponding anilide, toluidide, &c.

4':2:2'-Hydroxymethylethylquinazoline, from metamidoparatoluic acid and propionamide, crystallises in yellow needles and melts at  $240^{\circ}$ ; it dissolves freely in organic solvents, except ether, and in acids and alkalis. *Propionmetatoluidide*, which is formed at the same

time, crystallises in white needles, melts at  $81^{\circ}$ , and dissolves in organic solvents.

4':2-Hydroxyisopropylquinazoline, from anthranilic acid and isobutyramide, crystallises in white, lustrous needles, melts at  $224^{\circ}$ , and dissolves easily in benzene and alcohol, but sparingly in ether and water. Isobutyranilide (m. p.  $104^{\circ}$ ) is produced at the same time. 4':2:2'-Hydroxymethylisopropylquinazoline is obtained by substituting metamidoparatoluic acid for anthranilic acid. It crystallises in white needles, melts at  $228^{\circ}$ , and dissolves in organic solvents, acids, and alkalis. Isobutyrometatoluidide is formed at the same time; it crystallises in white needles, melts at  $85^{\circ}$ , and dissolves easily in alcohol, ether, chloroform, and benzene.

Bischler and Muntendam (this vol., i, 398) have named the compound obtained by the author from orthamidoparatoluamide and acetic anhydride,  $\alpha$ -hydroxy- $\beta$ -methylparatoluometadiazine; this is obviously incorrect, since the compound in question is the 4':2:2'-hydroxydimethylquinazoline described above. A. G. B.

**Amidoquinoxalinecarboxylic acid.** By A. PHILIPS (*Ber.*, 1895, 28, 1655—1657).—The author has previously shown that quinolinic acid may be converted by a series of reactions into amidopyridinecarboxylic acid (*Abstr.*, 1894, i, 301); he has now further subjected the analogous quinoxalinedicarboxylic acid to the same series of reactions, and finds that these proceed in the same manner, yielding as final product amidoquinoxalinecarboxylic acid. Quinoxalinedicarboxylic acid is readily converted into the anhydride  $C_8N_2H_4 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} O$

by boiling with acetic anhydride, and crystallises from this liquid in long, lustrous, pale brown needles, which melt and decompose at  $251^{\circ}$ . When gaseous ammonia is passed into the anhydride suspended in benzene, it is converted into the ammonium salt of the corresponding amide,  $NH_2 \cdot CO \cdot C_8N_2H_4 \cdot COONH_4$ , which crystallises from warm water in colourless needles, melting and decomposing at  $225^{\circ}$ . The free acid forms colourless needles, melts and evolves gas at  $183^{\circ}$ , again becoming solid, and then melts a second time at  $255^{\circ}$ ; on treatment with warm water, it takes up a molecule of water, forming the acid ammonium salt of quinoxalinedicarboxylic acid. To convert the acid into amidoquinoxalinecarboxylic acid, it is dissolved in dilute soda, treated with sodium hypobromite, and the excess of the latter removed by sulphurous acid.

Orthamidoquinoxalinecarboxylic acid,  $C_8H_4 \begin{smallmatrix} \text{N}:\text{C}:\text{NH}_2 \\ | \\ \text{N}:\text{C}:\text{COOH} \end{smallmatrix}$ , forms pale yellow needles, melts and decomposes at  $210^{\circ}$ , and is readily soluble in acids and bases, forming salts with both. When heated above its melting point, it gives off gas, yielding a brown basic product, which possibly contains amidoquinoxaline. H. G. C.

**A new Indicator—Luteol.** By WILHELM AUTENRIETH (*Arch. Pharm.*, 1895, 233, 43—48).—When ethoxydiphenylquinoxaline,  $OEt \cdot C_6H_5 \begin{smallmatrix} \text{N}:\text{C}:\text{Ph} \\ | \\ \text{N}:\text{C}:\text{Ph} \end{smallmatrix}$ , prepared by the action of benzile on metaethoxy-

phenylenediamine, is treated with phosphorus pentachloride (1 mol.), the corresponding monochlorinated derivative is obtained. After recrystallisation from alcohol, this *ethoxychlorodiphenylquinoxaline* forms yellowish, glistening needles, which melt at 146—147°. The correspond-

ing *hydroxychlorodiphenylquinoxaline*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl} < \begin{smallmatrix} \text{N}:\text{CPh} \\ | \\ \text{N}:\text{CPh} \end{smallmatrix}$ , obtained

when the ethoxy-derivative is hydrolysed with concentrated hydrochloric acid, crystallises from alcohol in yellowish, woolly needles, which melt at 246° and sublime at a higher temperature. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid, forming a deep red solution. It dissolves also in cold potassium, sodium, and ammonium hydroxides and carbonates, forming intense, yellow solutions, and thus possesses a much more strongly marked acid character than the hydroxydiphenylquinoxaline itself, which is slightly basic. The author recommends the use of this hydroxychlorodiphenylquinoxaline, or *luteol*, as an indicator in acidimetry and alkalimetry, as it is extremely sensitive. The solution is made by dissolving 1 gram of luteol in 300 c.c. of pure alcohol, and 3—8 drops of this solution is used for each titration. It is especially recommended for nitrogen estimations by Kjeldahl's method.

*Benzoylluteol*, prepared by the Schotten-Baumann method, crystallises in glistening, white plates, melts at 192°, and is insoluble in water, but readily soluble in hot alcohol and in ether.

*Acetyl luteol* obtained by heating luteol with acetic anhydride, crystallises in flat, glistening needles, melts at 185—186°, and is readily hydrolysed by hot sodium hydroxide solution. J. J. S.

**Formazyl Compounds.** By C. JAGERSPACHER (*Ber.*, 1895, 28, 1283—1287).—The nitrite of acetylamidrazonehydrazone,



(*Abstr.*, 1894, i, 98), when heated with light petroleum, yields three products. (1) Acetylamidrazonehydrazone, formed simply by loss of nitrous acid. (2) A substance which is isomeric with this hydrazone, and is perhaps a stereoisomeride; it crystallises in white, silky needles melting at 136°, and reacts with acetic acid at 250°, in the same way as the normal hydrazone, phenylamidomethylsotriazole being produced. (3) The third product is phenylazomethylsotriazole,  $\text{NPh} < \begin{smallmatrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C} \cdot \text{N}_2 \cdot \text{Ph} \end{smallmatrix}$ , formed by the elimination of water, ammonia,

and nitrogen. When phenylazomethylsotriazole is reduced, it is converted into amidomethylphenylsotriazole, identical with that obtained by the action of acetic acid on acetylamidrazonehydrazone. This substance can readily be diazotised, and yields a *diazoamidopiperidine* compound, which crystallises in yellow needles melting at 77°. When the diazo-solution is boiled, *hydroxymethylphenyltriazole*,

$\text{NPh} < \begin{smallmatrix} \text{N}:\text{C} \cdot \text{OH} \\ | \\ \text{N}:\text{CMe} \end{smallmatrix}$ , is produced, which melts at 140—142°, and is soluble

in alkalis. *Anilidomethyltriazole carbamide*,



forms slender, white needles melting at  $240^{\circ}$ . The corresponding thiocarbamide crystallises in flat, white, vitreous needles, and melts at  $195^{\circ}$ . *Methylphenyltriazolecarboxylic acid*,  $\text{NPh} \begin{smallmatrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C}\cdot\text{COOH} \end{smallmatrix}$ , prepared by Sandmeyer's reaction, crystallises in colourless needles melting at  $189^{\circ}$ . A. H.

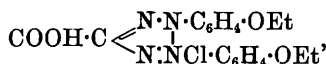
**Constitution of Tetrazolium Bases.** By HANS v. PECHMANN and EDGAR WEDEKIND (*Ber.*, 1895, 28, 1688—1695).—The preparation of tetrazolium bases by the oxidation of formazyl derivatives,  $\text{NHPH}\cdot\text{N}:\text{CR}\cdot\text{N}:\text{NPh}$ , has been previously described (*Abstr.*, 1894, i, 240; this vol., i, 74); attempts to synthesise similar compounds from tetrazine were unsuccessful, as this substance does not readily form additive compounds with alkyl haloïds. When tetrazolium derivatives are oxidised, the phenyl radicle is not eliminated, even when it contains sulphonic, amido-, or nitro-groups.

*Ethyllic diparaethoxyphenylformazylformate*,



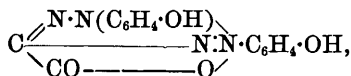
is prepared by the interaction of paradiazoethoxybenzene (2 mols.) and ethylic acetoacetate (3·5 mols.) in alkaline solution; it crystallises from alcohol in lustrous, dark red plates or needles with a blue reflex, melts at  $127\text{--}128^{\circ}$ , and dissolves in sulphuric acid with a bluish-green colour. The yield is about 53 per cent. of the ethylic acetoacetate employed.

*Diparaethoxyphenyltetrazoliumcarboxylic acid chloride*,



obtained by treatment of the preceding compound with amyllic nitrite and alcoholic hydrochloric acid, crystallises from hydrochloric acid, or from alcohol and ether containing hydrochloric acid, in colourless, lustrous prisms; it becomes yellow when heated, softens, and melts at  $194\text{--}195^{\circ}$ . It is quickly decomposed into the betaine (see below) by cold water. The yield is 60—70 per cent.

*Diparahydroxydiphenyltetrazoliumbetaine*,



is formed by boiling the above chloride with soda, or by heating with hydrobromic acid, but is best prepared by the action of fuming hydrochloric acid at  $140\text{--}145^{\circ}$ ; it crystallises with  $3\frac{1}{2}\text{H}_2\text{O}$  in colourless, hexagonal plates, melts and decomposes at  $178\text{--}179^{\circ}$ , and dissolves in alkalis with a reddish-yellow colour. The yield is 50—60 per cent. of the acid employed. When oxidised in dilute nitric acid solution with potassium permanganate, at a temperature not exceeding  $25^{\circ}$ , it is converted almost quantitatively into tetrazine, the silver salt of which crystallises from dilute nitric acid in prismatic needles,

which explode when heated. A direct proof is thus afforded of the constitution of the tetrazolium compounds.

*Diparaethoxyphenylformazylformic acid*,



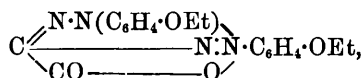
prepared from the ethylic salt (see above) by heating it with alcohol and soda during four minutes, is deposited from absolute alcohol in almost black plates with a blue reflex, from dilute alcohol in red needles; it melts at 147—148°.

*Ethylic diparaethoxyphenyltetrazoliumcarboxylate chloride*,



is obtained from the formazylformate, alcoholic hydrochloric, and nitrous acid at 0°; it is purified with difficulty, crystallises from a mixture of alcohol and ether in colourless prisms, melts at 187°, and is converted into the betaïne (see above) by the action of hydrochloric acid.

*Diparaethoxyphenyltetrazoliumbetaïne*,



prepared by the action of water or alkali carbonates on the preceding compound, crystallises with 2H<sub>2</sub>O in well developed, pale orange-yellow, hexagonal plates, melting at 113°.

*Diparahydroxyphenylformazylformic acid*,



is obtained by the reduction of the betaïne by means of sodium amalgam in alkaline solution; it crystallises from glacial acetic acid in dark green plates, melts at 186°, and gives an indigo-blue coloration with sulphuric acid.

*Ethoxybenzeneazoacetoacetic acid*,  $\text{COOH} \cdot \text{C} \cdot \text{Ac} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , is obtained as sodium salt in the preparation of ethylic diparaethoxyphenylformazylformate, from which it is separated by treatment with amyl nitrite and hydrochloric acid; it is less soluble than the latter compound, crystallises from alcohol in yellow prisms, melts at 172—173°, and dissolves in dilute alkalis and alkali carbonates. *Dimeta- and dipara-nitrophenylformazyl hydride*, prepared from malonic acid, meta-, and para-nitrodiazobenzene respectively in acetic acid solution, crystallise in brownish-red needles. *Ethylic dimetanitrophenylformazylformate*, from ethylic acetoacetate and metanitrodiazobenzene chloride in alkaline solution, is deposited in small, red needles melting at 217°. *Ethylic dimetanitrophenyltetrazoliumcarboxylate chloride*, prepared by the action of amyl nitrite and hydrochloric acid on the preceding compound, is deposited in slender, colourless crystals melting at 175—176°. *Diparamethoxyphenylformazyl hydride*, formed from malonic acid and paradiazomethoxybenzene acetate, crystallises in red prisms and melts at 88°.

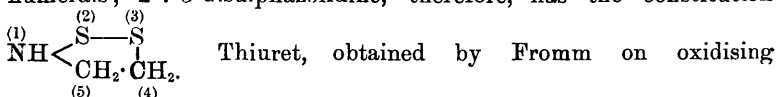
The formation of carbon-nitrogen compounds containing five atoms in the ring is not confined to the formazyl derivatives. Zincke has

obtained a triazolium base from benzeneazo- $\beta$ -naphthylphenylamine (this vol., i, 238), and the author has previously prepared compounds (ozotetrazones) with six atoms in the ring, but all attempts to obtain closed chains of three and four atoms,  $RC \begin{smallmatrix} \nwarrow NR \\ \nearrow NR \end{smallmatrix}$  or  $CH \begin{smallmatrix} \nwarrow N \\ \nearrow NR \end{smallmatrix} NR$ , have been fruitless.

J. B. T.

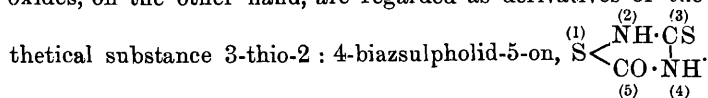
**Action of Bromine on Thiocarbimides.** By MARTIN FREUND (*Annalen*, 1895, **285**, 154—166).—An introduction to the two following papers. The action of bromine on aromatic and aliphatic thiocarbimides alike results in the formation of a mixture of the sulphide and oxide of the thiocarbimide employed, arising from the decomposition by water of the unstable intermediate products. If water, however, is excluded from the reaction, and the product, suspended in light petroleum, is submitted to the action of hydrogen sulphide, the sulphide alone is obtained, the oxide forming the sole product if water is present from the outset.

Disulphazolidine is the name proposed by the author for the ring composed of an imido-group, two sulphur atoms and two methylene groups, the relative position of the sulphur atoms being indicated by numerals; 2 : 3-disulphazolidine, therefore, has the constitution



$\alpha$ -phenyldithiobiuret with iodine (*Abstr.*, 1893, i, 575), has the constitution  $\text{NH} \begin{smallmatrix} \nwarrow \text{C}(\text{NPh}) \cdot \text{S} \\ \nearrow \text{C}(\text{NH}) - \text{S} \end{smallmatrix}$ , and is called 2-phenylimido-5-imido-3 : 4-disulphazolidine.

The sulphides dealt with in the following papers are either of this type or derived from 2 : 5-dimethylenetrisulphide,  $\text{S} \begin{smallmatrix} \nwarrow \text{CH}_2 \cdot \text{S} \\ \nearrow \text{CH}_2 \cdot \text{S} \end{smallmatrix}$ . The oxides, on the other hand, are regarded as derivatives of the hypo-



M. O. F.

**Action of Bromine on Methylthiocarbimide.** By MARTIN FREUND and ERNST ASBRAND (*Annalen*, 1895, **285**, 166—183).—

3-Thio-2 : 4-dimethylbiazsulpholid-5-on,  $\text{S} \begin{smallmatrix} \nwarrow \text{NMe} \cdot \text{CS} \\ \nearrow \text{CO} - \text{NMe} \end{smallmatrix}$ , is obtained

in the form of the tribromo-derivative,  $\text{C}_4\text{H}_6\text{N}_2\text{S}_2\text{OBr}_3$ , on adding a solution of bromine in chloroform to methylthiocarbimide in the same solvent, mixed with half its volume of alcohol. The tribromo-derivative crystallises in orange prisms, and melts at  $158^\circ$ . When exposed to air, or when treated with water, alcohol, acetone, sulphurous acid, or acetic anhydride, it is converted into the hydrobromide,  $\text{C}_4\text{H}_6\text{N}_2\text{S}_2\text{O} \cdot \text{HBr}$ , which crystallises from hot water in greenish-yellow needles, and melts at  $227^\circ$ . From this salt, the base is obtained by treatment with cold alkali; it crystallises in magnificent

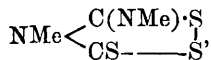
six-sided prisms, and melts at  $108^{\circ}$ . It dissolves sparingly in hot water, and is insoluble in cold, but is soluble in alcohol and ether, and dissolves very readily in chloroform; the base is volatile in an atmosphere of steam, and scarcely undergoes decomposition on distillation. The *hydrochloride* is colourless, and melts at  $223^{\circ}$ ; it becomes dissociated when the aqueous solution is boiled, resembling the hydrobromide in this respect. The *aurochloride* is yellow, and melts at  $182^{\circ}$ ; the *platinochloride* is a reddish-brown varnish, and the *mercurichloride* is a white, crystalline substance which melts at  $216^{\circ}$ . When reduced with ammonium sulphide in alcoholic solution, the base yields dimethylthiocarbamide, and a mixture of this substance with monomethylthiocarbamide is obtained on treating it with alcoholic ammonia; dimethylthiocarbamide melts at  $61^{\circ}$  (compare Hecht, Abstr., 1890, 477). The base is indifferent towards hydrochloric acid at  $100^{\circ}$ , but methylamine hydrochloride is obtained on heating it with the reagent for three hours at  $200^{\circ}$ . *Triphenylthiobiuret* is produced on boiling the solution of the base in aniline until the liquid acquires a brownish-black colour; hydrogen sulphide is liberated and sulphur is formed, whilst triphenylthiobiuret, which melts at  $234^{\circ}$ , crystallises out on allowing the solution to cool.

The *methylamine* salt of methylthiocarbamic acid,



is prepared by leading a current of carbon oxysulphide into an alcoholic solution of methylamine; it melts at  $120$ — $121^{\circ}$ , and forms colourless crystals, which become yellow and decompose in air. The action of oxidising agents gives rise to methylamine and sulphur.

1-*Methyl-2-methylimido-5-thio-3:4-disulphazolidine*,



results from the action of bromine on methylthiocarbimide and subsequent treatment of the product with hydrogen sulphide; it is also obtained by the action of bromine on the methylamine salt of methyl-dithiocarbamic acid dissolved in aqueous alcohol. It crystallises from alcohol in nacreous leaflets, and melts at  $86^{\circ}$ . The *tribromo-derivative*,  $\text{C}_4\text{H}_6\text{N}_2\text{S}_3\text{Br}_3$ , is an orange powder which yields the *hydrobromide*  $\text{C}_4\text{H}_6\text{N}_2\text{S}_3\cdot\text{HBr}$ , when heated; this salt forms yellow transparent crystals, and melts at  $248^{\circ}$ . The *hydrochloride* melts at  $227^{\circ}$ , and the *nitrate* melts and decomposes at  $130$ — $132^{\circ}$ ; the *sulphate* crystallises in long, six-sided prisms, and melts at  $221^{\circ}$ . The *tribromo-derivative* may be obtained by the action of bromine on *dimethylthiocarbamine bisulphide*,  $\text{NHMe}\cdot\text{CS}\cdot\text{S}\cdot\text{S}\cdot\text{SC}\cdot\text{NHMe}$ , which is prepared by adding bromine water to an aqueous, 33 per cent. solution of methylamine mixed with carbon bisulphide and alcohol, and agitating the liquid with ether; on evaporating the ether, a crystalline substance is obtained which melts and decomposes at  $109^{\circ}$ , and yields hydrogen sulphide and methylthiocarbimide when treated with boiling alcohol or water.

2: 5-*Dimethylimidodimethylenetrisulphide*,  $\text{S} < \begin{array}{c} \text{C(NMe)} \cdot \text{S} \\ \text{C(NMe)} \cdot \text{S} \end{array}$ , is isomeric

with 1-methyl-2-methylimido-5-thio-3:4-disulphazolidine, from which it is obtained by heating it at the melting point, and also by treating the alcoholic solution with potash, soda, ammonia, sodium ethoxide, or aniline. Treatment with alcoholic ammonia affords the most convenient method of preparation, and the substance is obtained in greenish, six-sided prisms which melt at 120°. The *bromo*-derivative melts at 127—128°; the hydrobromide (m. p. 248°) of the original base is obtained by treating the isomeride with boiling hydrobromic acid.

When 1-methyl-2-methylimido-5-thio-3:4-disulphazolidine is reduced in alcoholic solution with zinc dust and sulphuric acid, dimethylthiocarbamide is produced, but this substance has not been obtained by treating the isomeride with an acid or an alkaline reducing agent; when, however, it is heated with alcoholic ammonia for two hours at 100°, monomethylthiocarbamide is formed. On oxidising the base (m. p. 86°) with nitric acid (sp. gr. 1.16) methylamine nitrate is produced. Dimethylcarbamide is not present in the mixture of compounds obtained by treating the isomeride (m. p. 120°) in alcoholic solution with mercuric oxide.

M. O. F.

**Action of Bromine on Ethylthiocarbimide and Phenylthiocarbimide.** By MARTIN FREUND and GREGOR BACHRACH (*Annalen*, 1895, **285**, 184—203).—3-Thio-2:4-diethylbiazsulpholid-5-on,

$$\text{S} \begin{array}{c} \text{Net} \cdot \text{CS} \\ \text{CO} - \text{Net} \end{array}$$
, resembles the dimethyl derivative (preceding abstract)

in the method of its preparation; it melts at 45°, and crystallises in monoclinic plates, taking the form of long needles, when separation from the solvent is rapid. It is volatile in an atmosphere of steam, and is indifferent towards boiling water; the base boils without undergoing change. The *tribromo*-derivative crystallises in orange-red, six-sided prisms, and melts, undergoing decomposition at 180—181°; the *hydrobromide* forms slender, silky needles, and melts at 202°. The *hydriodide* and *hydrochloride* melt at 145° and 185° respectively; the *mercurichloride*,  $(\text{C}_6\text{H}_{10}\text{N}_2\text{SO}_2\text{HCl})_2 \cdot 3\text{HgCl}_2$ , crystallises in feathery aggregates of needles which melt at 131—132°, and the *aurochloride* melts at 167.5°. Reduction of the base gives rise to diethylthiocarbamide, and triphenylthiobiuret (*loc. cit.*) is obtained by the action of aniline.

1-Ethyl-2-ethylimido-5-thio-3:4-disulphazolidine,  $\text{Net} \begin{array}{c} \text{C(Net)S} \\ \text{CS} \end{array} \text{—S}^1$ ,

is obtained by adding a solution of bromine in light petroleum to ethylthiocarbimide in the same medium; the crystals which separate consist of the *hydrobromide* melting at 207°, and the base is obtained by decomposing this salt with soda after crystallisation from water. It separates from methylic alcohol in long, yellow needles, and melts at 29.5°; it boils without undergoing decomposition. The *hydrochloride* melts at 175°, the *nitrate* at 70—72°, and the *sulphate* at 176—178°. The base is also obtained from *diethylthiocarbamine bisulphide*,  $\text{NHet} \cdot \text{CS} \cdot \text{S} \cdot \text{S} \cdot \text{SC} \cdot \text{NHet}$ , which is prepared from the ethylamine salt of ethyldithiocarbamic acid by the action

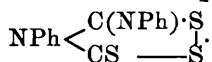


of bromine water; the bisulphide melts at 78—79°, and on treating the chloroform solution with bromine in the same medium, separation of ethylmethylimidothiodisulphazolidine takes place.

Alcoholic ammonia converts the base into ethylthiocarbamide, and diethylthiocarbamide is obtained on treating it with alcoholic ammonium sulphide; when heated with hydrobromic acid at 150—160°, sulphur, hydrogen sulphide, and ethylamine are produced. Attempts to obtain an isomeride analogous to dimethylimidodimethylenetri-sulphide (*loc. cit.*) were unsuccessful.

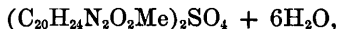
3-Thiodiphenyl-2 : 4-biazsulpholid-5-on,  $\text{S} \begin{smallmatrix} \text{NPh} \cdot \text{CS} \\ \text{CO} - \text{NPh} \end{smallmatrix}$ , is obtained in the form of the *hydrobromide* (m. p. 203°) by adding a chloroform solution of bromine to phenylthiocarbimide dissolved in chloroform mixed with alcohol; the base has been already described by Helmers (*Abstr.*, 1887, 581). The *hydrochloride* melts at 175°. Diphenylthiocarbamide is produced on reducing the base with alcoholic ammonium sulphide, and the action of boiling aniline results in the formation of triphenylthiobiuret.

1-Phenyl-2-phenylimido-5-thio-3 : 4-disulphazolidine,



has been already described (*Abstr.*, 1892, 984), and appears to be identical with phenyldithiocarbamic thioanhydride (Losanitsch, *Abstr.*, 1892, 55), because it can be obtained by treating ammonium phenyldithiocarbamate with a solution of bromine in light petroleum. It melts at 154—156°, and is not basic in character; alcoholic potash converts it into phenylthiourethane (m. p. 71—72°), and diphenylthiocarbamide is formed on reducing it with alcoholic ammonium sulphide. All attempts to prepare it from diphenylthiocarbamine disulphide have been unsuccessful. M. O. F.

**The Quinine Alkaloids.** By OSWALD HESSE (*Ber.*, 1895, 28, 1298—1302).—When quinine hydrate, in alcoholic solution, is treated with methylic iodide, quinine methiodide,  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2\text{MeI} + 2\text{H}_2\text{O}$ , is formed. The corresponding *sulphate* has the composition



whilst the *hydroxide* is a strongly basic, white mass. Boiling aqueous potash converts the methiodide into a substance which has been described by Claus and Mallman (*Ber.*, 14, 76) as methylquinine, but appears to be methylquinicine. The author proposes to confirm this view by preparing the methyl derivative of quinicine and comparing the two. A. H.

**Reduction of Cinchonine.** By FR. KONEK Edler v. NORWALL (*Monatsh.*, 1895, 16, 321—332).—On reduction in absolute alcoholic solution with sodium, cinchonine yields a dark yellow oil, soluble in ether, and drying to a gummy mass. This product is strongly basic, and gives a non-crystalline *sulphate* and a brownish-yellow, flocculent *platinochloride*, which appears to be a mixture of two (or more) com-

pounds,  $X_2H_2PtCl_6$  and  $X_2H_2PtCl_6$ , where X represents cinchonine or hydrocinchonine. From the gummy reduction products, amorphous substances have also been isolated; these soften at  $40-50^\circ$ , melt at  $60-80^\circ$ , and appear to have the composition of dihydrocinchonine.

On reduction in acetic acid solution with sodium, an oil is obtained, which is soluble in ether. It dissolves in hydrochloric acid, and, when fractionally precipitated with ammonia, yields yellow, amorphous masses of dihydrocinchonine,  $C_{19}H_{24}N_2O$ , and from this the dihydride,  $C_{19}H_{24}N_2O \cdot 2HI$ , was prepared in the form of reddish-yellow flocks.

When dissolved in concentrated hydrochloric acid solution and treated with metallic tin, cinchonine yields a molecular compound of cinchonine and cinchonine hydrochloride,  $C_{19}H_{22}N_2O \cdot C_{19}H_{23}N_2OCl$ . This crystallises from a mixture of benzene and alcohol in needles, melts at  $228^\circ$ , and, on trituration with hydrochloric acid, forms a sparingly soluble hydrochloride,  $C_{19}H_{23}ClN_2O \cdot 2HCl$ , from which König's hydrochlorocinchonine (*Ber.*, **20**, 2519) may be separated on the addition of soda. Zoin's chlorocinchonide (Hesse's hydrochloroäpocinchonine), obtained on heating cinchonine with hydrochloric acid at  $140-150^\circ$ , appears to be identical with the latter. G. T. M.

**Inosic acid.** By FRANZ HAISER (*Monatsh.*, 1895, **16**, 190—207).—The author shows that the inosic acid obtained by Liebig from meat extract contains phosphorus as one of its constituents. The acid was obtained from meat extract as the silver salt, and this was converted into the barium salt by precipitating the silver with hydrogen sulphide, and then treating with barium carbonate.

The *barium salt*,  $C_{10}H_{11}BaN_4PO_8 + 7\frac{1}{2}H_2O$ , crystallises in four-sided plates, which, when dry, have the appearance of polished silver. It loses  $6\frac{1}{2}H_2O$  at  $100-105^\circ$ , and the remaining  $H_2O$  when heated at  $100^\circ$  under diminished pressure.

An insoluble *basic barium salt* is formed when barium hydroxide is added to the aqueous solution of any salt of inosic acid. When dried at  $100^\circ$ , it has the composition  $Ba_3(C_{10}H_9N_4PO_8)_2 + 2H_2O$ .

The *calcium salt*,  $C_{10}H_{11}CaN_4PO_8 + 6\frac{1}{2}H_2O$ , forms colourless, transparent, monoclinic crystals, which are readily soluble in hot water.

The *potassium* and *ammonium* salts are very hygroscopic, and can be obtained in a crystalline form only with great difficulty. The acid itself,  $C_{10}H_{13}N_4PO_8$ , is decomposed when heated for some time in aqueous solution. The resulting products are sarkine, and two substances which could not be obtained quite pure, but are probably trihydroxyvaleric acid and trihydroxyvalerophosphoric acid. A similar decomposition occurs when inosic acid is treated with tin and hydrochloric acid. J. J. S.

## Organic Chemistry.

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**Double Salts of Silver and of Mercury containing Cyanogen.** By F. W. SCHMIDT (*Zeit. anorg. Chem.*, 1895, 9, 418—433).—Long, well-developed crystals are obtained when ammoniacal mercuric cyanide solution is allowed to remain for a considerable time at low temperatures. The compound is unstable, and at the ordinary temperature dissolves in the mother liquor, crystals of ammoniomercuric cyanide,  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$ , being formed; this has been previously prepared in a different manner by Varet. Silver nitrate solution, when mixed with saturated mercuric cyanide solution, gives a sparingly soluble, crystalline, additive compound,



which explodes when heated, but with more dilute solutions, or in presence of nitric acid, no precipitate is formed. The compounds  $\text{CN} \cdot \text{HgNO}_3$ ,  $\text{OH} \cdot \text{HgNO}_3$ ,  $10\text{AgCN}$  and  $\text{OH} \cdot \text{HgNO}_3$ ,  $20\text{AgCN}$ ,  $5\text{Ag}_2\text{O} + 7\text{H}_2\text{O}$  are formed by mixing a cold saturated ammoniacal mercuric cyanide solution with 5 and 2 parts respectively of aqueous silver nitrate (10 per cent.); both are colourless, amorphous, pulverulent, and sparingly soluble, but do not explode when heated. When the above solutions are mixed in the proportion of 1 : 0.3—1.2 of silver nitrate, pure silver cyanide is precipitated; the further addition of silver nitrate causes a steady decrease of silver in the precipitates. The compound  $\text{OH} \cdot \text{HgNO}_3 \cdot \text{AgCN} \cdot 2\text{H}_2\text{O}$  is obtained in crystals when ammoniacal mercuric cyanide solution (25 c.c.) is mixed with water (225 c.c.) acidified with nitric acid, and silver nitrate (100 c.c.) added; it explodes violently when heated. By the interaction of silver nitrate (7.5 grams), water (7.5 grams), concentrated ammonia (30 c.c.), and ammoniacal mercuric cyanide (20 c.c.), a compound,  $2\text{OH} \cdot \text{HgNO}_3 \cdot 2\text{AgCN} \cdot 4\text{Ag}_2\text{O} \cdot 3\text{NH}_4\text{CN}$ , is formed, which crystallises in plates, and explodes slightly when heated. The compound  $4\text{OH} \cdot \text{HgCN} \cdot 3\text{AgCN} \cdot 2\text{Ag}_2\text{O} \cdot \text{NH}_4\text{CN} + \frac{1}{2}\text{H}_2\text{O}$  is formed like the preceding salt, if the silver nitrate is first precipitated with soda and the oxide dissolved in concentrated ammonia (50 c.c.). It is yellow, pulverulent, and somewhat unstable, but does not explode when heated. In all the above experiments, a cold, saturated solution of ammoniacal mercuric cyanide, and a 10 per cent. solution of silver nitrate, were employed. For the analysis of the above compounds, the mercury was determined as sulphide, the silver precipitated as chloride and cyanide, converted into sulphide by means of ammonia and ammonium sulphide, and this into metal by cautious roasting.

Potassium triiodide and silver nitrate in aqueous or alcoholic solution give a dark brown precipitate, which probably consists of *silver triiodide*,  $\text{AgI}_3$ ; it is unstable, and readily dissolves in excess of potassium triiodide. Iodine added to highly dilute ammoniacal silver nitrate

solution gives a white, flocculent precipitate, which becomes yellow when dry, and is possibly silver hypoiodite. J. B. T.

**Bimolecular Nitriles and their Derivatives.** By ERNST V. MEYER (*J. pr. Chem.*, 1895, [2], 52, 81—117; compare *Abstr.*, 1888, 802; 1889, 113, 114, 683, 684; 1893, i, 314).—On one occasion, when benzene was used instead of ether as a solvent in the preparation of diacetonitrile, the product was found to melt at 74—76°, but after it had been kept at 80° for some time the melting point fell to that of diacetonitrile (52°). This *labile* or  $\alpha$ -diacetonitrile has been heretofore overlooked, because the product of the action of sodium on acetonitrile has always been crystallised from boiling benzene, a process which converts the labile into the *stable* or  $\beta$ -diacetonitrile;  $\alpha$ -diacetonitrile melts at 79—84°, and is only about one-seventh as soluble in benzene as the stable form is, so that it remains undissolved when a mixture of the  $\alpha$  and  $\beta$  forms is treated with benzene at 35°. In the following experiments,  $\beta$ -diacetonitrile was used.

*Chlorodiacetonitrile*,  $\text{NCl}:\text{CMe}:\text{CH}_2:\text{CN}$  (?), is obtained when diacetonitrile is treated with chloride of lime and the product extracted with ether; it crystallises in white needles, and melts at 120°. The corresponding *bromo-derivative* is obtained as a white precipitate when diacetonitrile is agitated with excess of bromine dissolved in potash; it crystallises in colourless needles and melts at 123°. The halogen cannot be removed from either compound by the ordinary reagents.

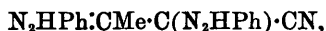
By heating diacetonitrile with ethylic chlorocarbonate at 100° and extracting the product with ether, a compound,  $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_3$ , is dissolved, and a white salt is left. The former crystallises in white laminæ and melts at 84°. The latter contains chlorine, and when heated with dilute potash yields ammonia and a white residue consisting of Holtzwardt's base,  $\text{C}_8\text{H}_9\text{N}_3$  (*Abstr.*, 1889, 683); this base is very sparingly soluble in water, ether, and benzene, but more freely in alcohol; its *platinochloride*,  $(\text{C}_8\text{H}_9\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in sparingly soluble, thin, bright yellow prisms. With acetic anhydride, the base yields a *monacetyl derivative*,  $\text{C}_8\text{H}_8\text{N}_3\text{Ac}$ , which melts at 250°. The base is easily formed from diacetonitrile when this is placed under conditions favourable for the separation of ammonia without access of water, such, for instance, as when it is heated in boiling ethylenic bromide. An *isomeride*, melting at 157°, is obtained when diacetonitrile is treated with carbonyl chloride and the chlorinated product is suspended in water made feebly alkaline with ammonia; when heated with potash, it is converted into Holtzwardt's base (m. p. 222°). By treatment with nitrous acid, the isomeric base yields a compound,  $\text{C}_8\text{H}_8\text{N}_2\text{O}$ , similar in composition to that which Holtzwardt obtained by heating diacetonitrile with water (*loc. cit.*); but it crystallises in small needles, decomposes above 260°, and dissolves to the extent of 0.09 gram in 100 c.c. of alcohol (at 16°), and of 0.042 gram in 100 c.c. of water (at 16°), whilst Holtzwardt's compound crystallises in long, lustrous needles, blackens at 230°, and dissolves to the extent of 0.54 gram in 100 c.c. of alcohol (at 16°), and of 0.05 gram in 100 c.c. of water (at 16°). Neither compound combines

with hydroxylamine or phenylhydrazine. The author discusses the constitution of the above substance, but arrives at no conclusion.

The *hydrochloride*,  $C_4H_8N_2 \cdot HCl$ , was obtained as an amorphous, white precipitate on passing hydrogen chloride into a benzene solution of diacetonitrile. With carbanil in a benzene solution, both  $\alpha$ - and  $\beta$ -diacetonitrile yield three compounds: (1) needles,  $C_{11}H_{11}N_3O$ , which melt at about  $121$ – $122^\circ$ ; (2) laminæ, which melt at about  $150^\circ$  and are also obtained when (1) is dissolved in hydrochloric acid and reprecipitated by an alkali; (3) a crystalline powder which melts at  $229^\circ$ ; all three have the same percentage composition.

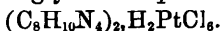
Diacetonitrile reacts with cyanamide in warm water, with separation of ammonia and formation of a *condensation product*,  $C_9H_{10}N_4O$ , which crystallises in needles and melts and decomposes at about  $145^\circ$ ; when heated with water, it yields the compound  $C_8H_8N_2O$ .

With diazobenzene chloride, diacetonitrile yields the *phenylhydrazone*,  $NH \cdot CMe \cdot C(N_2HPh) \cdot CN$ , which readily passes into *cyanacetone-phenylhydrazone*,  $COMe \cdot C(N_2HPh) \cdot CN$ ; the latter crystallises in yellow, silky needles, and melts at  $166$ – $167^\circ$ . The two compounds combine to form an additive product,  $C_{20}H_{19}N_7O$ , which crystallises in yellow needles and melts at  $165^\circ$ . The *osazone*,



was prepared; it melts at  $162$ – $170^\circ$ . Methylisoxazolenimide (Abstr., 1893, 314) and diazobenzene chloride yield the corresponding *phenylhydrazone*,  $N \leq \overline{CMe \cdot C(N_2HPh)} > C \cdot NH$ , which melts and partially decomposes at  $119^\circ$ , and is converted by acids into Knorr's keto-methylisoxazalone phenylhydrazone (Abstr., 1894, i, 372).

When diacetonitrile (1 mol.), dissolved in the smallest possible quantity of warm water, is added to a solution of hydrazine sulphate ( $1\frac{1}{2}$  mols.) in dilute ammonia, white needles (A) separate in the course of 12 hours; if the mother liquor is neutralised with hydrochloric acid, a further precipitation of white needles (B) occurs. These compounds,  $C_8H_{10}N_4$ , are isomerides. The substance A melts at  $85^\circ$ , and dissolves easily in dilute hydrochloric acid, but not in alkalis; hot, strong hydrochloric acid partly decomposes it with separation of ammonia, and partly converts it into a third isomeride; treatment with hot alkali causes it to evolve ammonia. The substance B melts at  $105^\circ$  (at  $107^\circ$  after crystallisation from benzene), and is more soluble in water, but less soluble in benzene and in dilute hydrochloric acid than A is; strong hydrochloric acid dissolves it, but without decomposition, for alkalis precipitate it from the solution in the form of the third isomeride; it reduces silver nitrate. The third isomeride crystallises in needles, melts at  $200$ – $201^\circ$ , and is freely soluble in hot water, but only sparingly so in benzene; it is the most stable of the three isomerides, and yields a sparingly soluble *platinochloride*,

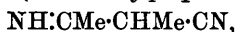


The reaction of A with nitrous acid yields a compound,  $C_7H_8N_4$ , crystallising in rhombic prisms, which melt and decompose at  $213^\circ$ . Diazobenzene sulphate reacts with B to form cyanacetonephenylhydrazone. The constitution of these isomerides remains unknown.

A condensation product,  $C_{15}H_{13}N_3$ , is obtained on adding concentrated hydrochloric acid to benzaldehyde ( $1\frac{1}{2}$  mols.) and diaetonitrile (1 mol.) dissolved in glacial acetic acid; it crystallises in white needles, melts at  $205-206^\circ$ , and dissolves sparingly in ether and benzene, but not in water. If the action takes place in alcoholic solution in presence of sodium ethoxide, the product melts at  $201-202^\circ$ , but is converted into the above compound by dilute sulphuric acid.

Dipropionitrile (Abstr., 1889, 114, 841) is a far less active compound than diacetonitrile, and enters into reaction with diazobenzene chloride alone of the reagents mentioned above. The compound,  $C_{12}H_{14}N_4$ , thus formed, crystallises in microscopic, yellow prisms, and melts at  $151^\circ$ .

*Acetopropionyl dinitrile (imidoacetylepropionitrile),*



prepared from a mixture of methylic and ethylic cyanide in the manner adopted for diacetonitrile, forms crystals, which melt at  $113^\circ$ . Its benzoyl derivative,  $C_6H_5BzN_2$ , crystallises in white needles, and melts at  $98-100^\circ$ .

Benzacetodinitrile,  $NH:CPh\cdot CH_2\cdot CN$ , combines with carbanil to form an additive compound, which crystallises in needles, melts at about  $192^\circ$ , and is not soluble either in acids or in alkalis. By saturating an alcoholic solution of benzacetodinitrile with hydrogen chloride, a compound,  $C_{18}H_{12}N_2O$ , analogous to that formed by heating diacetonitrile with water, is obtained; this crystallises in long, white needles, and melts at  $144^\circ$ .

*Cyanacetophenonephenylhydrazone*,  $COPh\cdot C(N_2HPh)\cdot CN$ , is the product of the reaction between benzacetodinitrile and diazobenzene chloride; it crystallises in yellow needles, melts at  $135^\circ$ , dissolves in ammonia, and yields a silver derivative.

With benzaldehyde, benzacetodinitrile yields *benzylidenbenzacetodinitrile*,  $\begin{matrix} PhCN \\ | \\ CN\cdot CH \end{matrix} > CHPh$ , which crystallises in rhombic laminæ, and melts at about  $260^\circ$ ; it is insoluble in water, and only sparingly soluble in ether and in alcohol.

By the action of nitrous acid on benzacetodinitrile, a *nitrite*, crystallising in needles and melting at  $151^\circ$ , is formed; this loses nitrous acid when treated with hydrochloric acid, yielding *isonitrosocyanacetophenone*,  $COPh\cdot C(NO\ddot{H})\cdot CN$ , which forms stellate groups of crystals, and melts at  $122^\circ$ ; its silver compound was prepared.

Benzopropiodinitrile (imidobenzoyl ethyl cyanide (Abstr., 1889, 577)), yields the compound,  $C_{10}H_{10}N_2O$ , when treated with hydroxylamine; the new substance crystallises in needles, and melts at  $92^\circ$ .

*Paratoluacetodinitrile*,  $NH:C(C_6H_4Me)\cdot CH_2\cdot CN$ , from methylic cyanide and paratolylic cyanide, crystallises in broad prisms, melts at  $108^\circ$ , and dissolves sparingly in hot water, but freely in ether and benzene. When heated with dilute hydrochloric acid, it is converted into *cyanomethyl paratolyl ketone*,  $C_6H_4Me\cdot CO\cdot CH_2\cdot CN$ , which crystallises in slender prisms, and melts at  $104-105^\circ$ ; the corresponding *oxime* melts at  $150-151^\circ$ . With phenylhydrazine, paratoluaceto-

dinitrile yields laminæ, which melt at  $169^{\circ}$ , and are too stable to be a phenylhydrazone. *Bromoparatoluacetodinitrile* melts at  $164^{\circ}$ , and *chloroparatoluacetodinitrile* at  $149^{\circ}$ . The *benzoyl* derivative of paratoluacetodinitrile melts at  $179^{\circ}$ , and the *benzylidene* derivative (see above) melts and decomposes at  $215^{\circ}$ . *Cyanomethyltolylketone phenylhydrazone*, from diazobenzene chloride and paratoluacetodinitrile, melts at  $152-153^{\circ}$ .

*Paratolupropiodinitrile*,  $\text{NH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CHMe}\cdot\text{CN}$ , from paratolylic cyanide and ethylic cyanide, melts at  $98-99^{\circ}$ ; with hydroxylamine it yields, not the appropriate ketoxime (see above), but the isomeric *isoxazonimide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ , which crystallises in white prisms, and melts at  $134^{\circ}$ .

*Diphenacetoneitrile*,  $\text{NH}\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CHPh}\cdot\text{CN}$ , from benzylic cyanide, is an oil which was identified by the fact that it yielded the same *oxime* (m. p.  $107^{\circ}$ ) as that obtained from  $\alpha$ -cyanophenylmethyl benzyl ketone,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CN}$ ; this ketone is prepared by the condensation of ethylic phenylacetate and benzylic cyanide in the presence of sodium ethoxide; it melts at  $85-86^{\circ}$ , and is converted by gaseous ammonia at  $170^{\circ}$  into diphenacetoneitrile.

*Benzophenacetodinitrile*,  $\text{NH}\cdot\text{CPh}\cdot\text{CHPh}\cdot\text{CN}$ , prepared by the action of gaseous ammonia at  $170^{\circ}$  on the corresponding ketone (see below), crystallises in laminæ and melts at  $146^{\circ}$ .  $\alpha$ -Cyanodeoxybenzoïn,  $\text{COPh}\cdot\text{CHPh}\cdot\text{CN}$ , prepared by the condensation of ethylic benzoate with benzylic cyanide in presence of sodium ethoxide, melts at  $87-90^{\circ}$ .

A. G. B.

**Ethenylic Trisulphide.** By P. CANDIANI (*Gazzetta*, 1895, 25, i, 81-88).—Ethenylic trisulphide is conveniently prepared by the action of bromine vapour on thioacetic acid in a closed tube at ordinary temperatures; the action is an indirect one, the trisulphide being produced by the agency of the hydrogen bromide which is evolved, for on sealing up thioacetic acid in a tube with an arrangement by which water is caused to act on phosphorus bromide, thus liberating hydrogen bromide under pressure, ethenylic trisulphide is obtained. Cryoscopic determinations in benzene solutions show that the substance has the molecular formula  $\text{C}_2\text{H}_2\text{S}_6$ . For 9.9-11.5 per cent. benzene solutions at  $15.9^{\circ}$ , the molecular refractions are 137.34 and 77.66, and the atomic refractions of sulphur are 13.58 and 7.53 for the  $\alpha$ -hydrogen ray, calculating by the empirical and theoretical formulæ respectively. These values of the atomic refractions approximate closely to those deduced from the refraction constants of ethylic sulphide.

Bromine acts on an ethereal solution of thioacetic acid, yielding a dense, oily substance, which fumes in the air and slowly loses hydrogen bromide during distillation under reduced pressure; it seems to have the composition  $\text{C}_6\text{H}_{10}\text{Br}_2\text{SO}_2$ .

W. J. P.

**Optically Active Halogen Derivatives.** By J. ACHILLE LE BEL (*Ber.*, 1895, 28, 1923-1924).—The author points out that Walden, in his recent paper having the above title (this vol., i, 450), makes no mention of a previous paper of the author's (*Abstr.*, 1894, ii, 77), in

which the same question was discussed and a number of the same active halogen derivatives described. Thus the author also obtained the active methylic salt of sarcosolactic acid, and converted it into the acetin and butyrin, which are lævo-rotatory, whilst Walden's chlorhydrin and bromhydrin are dextro-rotatory, the relation of these compounds being the same as with the corresponding derivatives of secondary amylic alcohol. On the other hand, the active monochlorhydrin of propylene glycol,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , behaves in a totally different manner, as when the hydroxyl is displaced by chlorine the sign of rotation remains unchanged, but changes when hydroxyl is displaced by the acetoxy-, chloracetoxy-, or butyroxy-groups. It is evident, therefore, that halogen derivatives form an exception to Guye's hypothesis.

H. G. C.

**The Multirotation of Dextrose.** By A. LEVY (*Zeit. physikal. Chem.*, 1895, **17**, 301—324).—The retrogression of the multirotation of a solution of dextrose is accelerated by the addition of small quantities of acids or strong bases, and the author conducted a series of experiments to determine the comparative effects, in this respect, of various compounds at various concentrations. In these determinations, the half shadow apparatus of Schmidt and Haensch was employed, the tube being 80 mm. long, and although this length of tube minimises the errors consequent on the use of a short tube, it has many manipulative disadvantages. The value of the velocity of retrogression was obtained from the equation  $C = 1 \div (t_2 - t_1) \times \log \{ \beta_1 - \phi \} / \{ \beta_2 - \phi \}$  where  $\phi$  is the final rotation and  $\beta_1$  and  $\beta_2$  that after times  $t_1$  and  $t_2$ , a form of expression which does not necessitate a knowledge of the absolute values of  $t_1$  and  $t_2$ . The values so obtained with pure water are 0.00637 ( $T = 20.25^\circ$ ) and 0.00610 ( $T = 20.1$ ). Researches are next recorded with acetic, propionic, sulphuric, nitric, hydrochloric, chloracetic, dichloracetic, and trichloracetic acids in N/10, and frequently, also, N/50 solutions. The velocity is found to be dependent on the nature and concentration of the acid, and the intimate connection between this effect of the acid and its affinity constant is seen in the accompanying table.

Acid.	1.	2.	3.	4.
Hydrochloric.....	100.00	100.0	100.0	100.0
Nitric.....	98.99	99.6	91.0	100.0
Trichloracetic.....	96.67	62.3	68.2	75.4
Sulphuric..	71.95	65.1	73.9	73.2
Dichloracetic.....	62.41	25.3	23.0	27.1
Monochloracetic.....	17.25	4.9	4.3	4.84
Acetic.....	4.70	1.42	0.345	0.4
Propionic.....	1.63	0.32	0.304	—

1 is the effect on multirotation; 2, electrical conductivity; 3, catalysis of methylic acetate; 4, inversion of cane sugar.

Alcohol, as expected, causes a decrease of the velocity, as does also sodium chloride; sodium sulphate, however, causes a marked increase,



due, the author considers, to a partial decomposition,  $\text{Na}_2\text{SO}_4 + \text{OH}_2 = \text{NaHSO}_4 + \text{NaOH}$ , this view being further supported by the great accelerating influence of sodium salts of feeble acids, such as sodium acetate. Strong bases cause so rapid a decrease of the rotation that they are practically unmeasurable; ammonia, however, was measured, and found to cause an acceleration, but not as great as that due to strong acids. L. M. J.

**Combination of Iodine with Potato Starch.** By GASTON ROUVIER (*Compt. rend.*, 1895, **120**, 1179—1180).—The maximum quantity of iodine with which potato starch will combine is 18·6 per cent., even when the iodine is present in very large excess. In the case of wheat and rice starch, the maximum is 19·6 per cent. In presence of water, the potato starch combines with only 13·5 per cent. of the iodine, the corresponding number in the case of wheat and rice being about 8·9. When the quantity of iodine added to a given weight of starch is gradually increased, the proportion entering into combination also gradually increases up to the maximum, but the variations are less rapid than with wheat starch and rice starch (*Abstr.*, 1894, i, 63 and 353).

It would seem that whilst starches of the same class, such as wheat starch and rice starch, behave similarly in contact with iodine, starches derived from plants belonging to different families behave very differently. C. H. B.

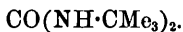
**Oxidation of Complex Carbohydrates.** By GUILLAME DE CHALMOT (*Amer. Chem. J.*, 1895, **17**, 535—539).—The action of soda and bromine on certain carbohydrates was tried. From starch, a product is formed which reduces Fehling's solution in the cold; cellulose yields apparently an oxycellulose which reduces Fehling's solution at 100°; the products obtained from saccharose and from  $\alpha$ -methyl-*d*-glucoside gave respectively glucosazone and a substance which was the osazone either of  $\alpha$ -methyl-*d*-glucoside or of *d*-glucose. C. F. B.

**Aliphatic Nitramines.** By H. VAN ERP (*Rec. Trav. Chim.*, 1895, **14**, 1—55).—A study of the butylnitramines and normal hexylnitramines. The starting point in each case was the corresponding monalkylamine, which was converted into the methylic or ethylic alkylcarbamate, and the latter nitrated; the alkyl nitrocarbamate was then decomposed with ammonia, and the ammonium derivative of the nitramine thus formed was decomposed by dilute sulphuric acid.

Normal butylamine was prepared by reducing butyronitrile with sodium in alcoholic solution, the nitrile being obtained by the successive distillation of butyric acid with ammonium thiocyanate, and of the resulting product with phosphoric anhydride. The tertiary butylamine and the hexylamine were made respectively from trimethylacetamide and normal heptoamide by the action of bromine and alkali, the trimethylacetic acid being obtained by oxidising pinacolone with chromic acid. Normal hexylamine may be characterised by means of *dinitrohexylaniline*,  $\text{C}_6\text{H}_5(\text{NO}_2)_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{13}$ , from 1 : 2 : 4-bromodinitrobenzene, and by the corresponding *trinitro-compound*

from picryl chloride. The former compound crystallises in long, slender, yellow needles, and melts at  $38.2-39.2^\circ$ , whilst the latter forms large, yellow, doubly-refracting plates belonging to the asymmetric system, and melts at  $70-70.5^\circ$ ;  $\alpha = 91^\circ 56'$ ;  $\beta = 124^\circ 10'$ ;  $\gamma = 82^\circ 54'$ .

A bye-product obtained in the preparation of the tertiary butylamine was probably *symmetrical ditertiarybutylcarbamide*,



This is a micro-crystalline powder insoluble in water, but soluble in alcohol and ether; it sublimes at  $250^\circ$  without melting.

The carbamates were obtained by adding methylic or ethylic chlorocarbamate to a mixture of the respective amines with aqueous potash, and extracting the product with ether. They are colourless, viscid liquids, having for the most part faint, ethereal odours. The yields were good. *Methylic butylcarbamate*,  $\text{NHBu}\cdot\text{COOMe}$ , melts at  $-18.5^\circ$  to  $-17.5^\circ$ , and boils at  $92^\circ$  (15 mm.); sp. gr. = 0.974 at  $15^\circ$ ; the *ethylic* salt melts at  $-22.5^\circ$  to  $-21.5^\circ$ , and boils at  $100^\circ$  (15 mm.); sp. gr. = 0.951 at  $15^\circ$ . *Methylic secondary butylcarbamate*,  $\text{CHMeEt}\cdot\text{NH}\cdot\text{COOMe}$ , boils at  $83^\circ$  (16 mm.); sp. gr. = 0.972 at  $15^\circ$ ; the *ethylic* salt melts at  $-14^\circ$  to  $-13^\circ$  and boils at  $89.8^\circ$  (15 mm.); sp. gr. = 0.9495 at  $15^\circ$ . *Methylic isobutylcarbamate*,  $\text{CH}_2\text{Pr}^\beta\cdot\text{NH}\cdot\text{COOMe}$ , melts at  $-23.5^\circ$  to  $-21^\circ$ , and boils at  $89^\circ$  (18 mm.); sp. gr. = 0.9695 at  $15^\circ$ ; the *ethylic* salt boils at  $96^\circ$  (17 mm.), and does not solidify at  $-65^\circ$ ; sp. gr. = 0.9465 at  $15^\circ$ . *Methylic tertiary butylcarbamate*,  $\text{CMe}_3\cdot\text{NH}\cdot\text{COOMe}$ , melts at  $26.7-27.2^\circ$ , and boils at  $63.3^\circ$  (17 mm.); sp. gr. = 0.966 at  $15^\circ$ ; the *ethylic* salt melts at  $20.5-22^\circ$ , and boils at  $72^\circ$  (16 mm.); sp. gr. = 0.943 at  $15^\circ$ ; the odour of both these salts resembles that of menthol. *Ethylic hexylcarbamate*,  $\text{C}_6\text{H}_{13}\cdot\text{NH}\cdot\text{COOEt}$ , boils at  $232-234^\circ$  (uncorr.), and has sp. gr. = 0.915 at  $15^\circ$ ; the melting point of a second preparation, sp. gr. = 0.9231 at  $15^\circ$ , was  $-6.7^\circ$ .

The nitrocarbamates are prepared by adding the carbamates to concentrated nitric acid at  $0^\circ$ , or, in some cases, at still lower temperatures; the product is poured on to a mixture of sodium carbonate crystals and ice, and the oily carbamate taken up with ether. There is no oxidation in the case of the primary and isopropyl compounds, but the secondary butyl derivatives are prepared only with great difficulty, and the tertiary compound could not be prepared at all. The yields were almost theoretical. The nitrocarbamates are nearly colourless, oily liquids of faint ethereal or aromatic odour. They solidify at low temperatures to crystalline or porcelain-like masses, and apparently cannot be distilled without decomposing. *Methylic butylnitrocarbamate*,  $\text{NO}_2\cdot\text{NBu}\cdot\text{COOMe}$ , melts at  $-35.2^\circ$  to  $-34.2^\circ$ ; sp. gr. = 1.149 at  $15^\circ$ ; the *ethylic* salt is still liquid at  $-70^\circ$ ; sp. gr. = 1.1055 at  $15^\circ$ . *Methylic secondary butylnitrocarbamate*,  $\text{CHMeEt}\cdot\text{N}(\text{NO}_2)\cdot\text{COOMe}$ , becomes viscid at  $-70^\circ$ ; sp. gr. = 1.1355 at  $15^\circ$ ; the *ethylic* salt remains liquid at  $-70^\circ$ ; sp. gr. = 1.094 at  $15^\circ$ . *Methylic isobutylnitrocarbamate*,  $\text{CH}_2\text{Pr}^\beta\cdot\text{N}(\text{NO}_2)\cdot\text{COOMe}$ , melts at  $2^\circ$ ; sp. gr. = 1.144 at  $15^\circ$ ; the *ethylic* salt becomes very slightly viscid at  $-75^\circ$ ; sp. gr. = 1.101 at  $15^\circ$ . *Ethylic hexylnitro-*

carbamate,  $C_6H_{13}N(NO_2) \cdot COOEt$ , solidifies at  $-60^\circ$ , and melts at  $-45^\circ$  to  $-40^\circ$ ; sp. gr. = 1.062 at  $15^\circ$ .

The nitramines are prepared by saturating the dry, ethereal solutions of the methylic or ethylic nitrocarbamates with dry ammonia, the resulting crystalline ammonium salt of the nitramine being decomposed with dilute sulphuric acid, and the amine separated partly mechanically and partly by extraction with ether; the yield was in most cases almost theoretical. The nitramines are colourless, somewhat viscid liquids, having little odour; they are only sparingly soluble in water, but easily in the usual organic solvents; the aqueous solutions are alkaline to litmus. They readily dissolve in alkalis, forming salts from which various metallic and alkylic salts can be prepared. It is noteworthy that both butyl- and isobutyl-nitramines form two methylic derivatives, to which apparently the same structure must be assigned. *Butylnitramine*,  $NHBu \cdot NO_2$ , melts at  $-0.5^\circ$  to  $+0.5^\circ$ ; sp. gr. = 1.0665 at  $15^\circ$ ; the ammonium derivative crystallises in small, white, glistening scales, and superficially dissociates in air into its proximate constituents; the *potassium*, *barium*, and *silver* derivatives are crystalline. The two *methyl* derivatives are prepared respectively from the potassium compound by the action of methylic iodide and methylic alcohol, and from the silver derivative by means of methylic iodide in ethereal solution.  *$\alpha$ -Methylbutylnitramine*,  $NMeBu \cdot NO_2$ , has an odour of menthol; it boils at  $107.7^\circ$  (15 mm.), and is still liquid at  $-30^\circ$ ; sp. gr. = 1.031 at  $15^\circ$ ;  *$\beta$ -Methylbutylnitramine*,  $NMeBu \cdot NO_2$  (?), has, on the other hand, a very pungent odour; it boils at  $75-88^\circ$ ; sp. gr. = 0.9865 at  $15^\circ$ . *Secondary butylnitramine*,  $CHMeEt \cdot NO_2$ , melts at  $-34.5^\circ$  to  $-33^\circ$ ; sp. gr. = 1.066 at  $15^\circ$ ; the ammonium, barium, and silver derivatives are crystalline, but neither the *potassium* nor the sodium derivative could be crystallised; the former is very hygroscopic. *Isobutylnitramine*,  $CH_2Pr^s \cdot NH \cdot NO_2$ , is a white, crystalline substance, and melts at  $32.2^\circ$ ; sp. gr. = approximately 1.142; the ammonium and silver derivatives are crystalline; the *potassium* derivative crystallises with 1 mol.  $H_2O$ , which it loses at  $125^\circ$ , and the anhydrous compound decomposes at  $245^\circ$  without melting. The two *methylic* derivatives were prepared in the same way as those of the normal butyl derivatives;  *$\alpha$ -methylisobutylnitramine* forms small, colourless crystals, and resembles the corresponding normal compound in odour; it melts at  $22.4^\circ$ , and boils at  $104-104.2^\circ$  (17 mm.).  *$\beta$ -Methylisobutylnitramine* also resembles the corresponding normal compound in odour; it boils at  $63-66^\circ$  (17 mm.), and is still liquid at  $-20^\circ$ .

*Hexylnitramine*,  $C_6H_{13} \cdot NH \cdot NO_2$ , melts at  $5.5-6.5^\circ$  to a colourless liquid, of sp. gr. = 1.014 at  $15^\circ$ ; the ammonium derivative forms colourless, greasy scales, and is very soluble in water; the *potassium* derivative is crystalline, and commences to melt at  $230^\circ$ , but the melting is not complete at the temperature,  $280^\circ$ , at which decomposition sets in. The *silver* and *cobalt* derivatives are crystalline.

The specific gravities of the alkyl nitramines and nitrocarbamates, as of other homologous compounds, diminish as the series is ascended; the relations between the melting points of the various isomeric butyl compounds are normal.

Hexylnitramine is completely decomposed by dilute sulphuric acid into two hexylic alcohols, a hexylic ether, a hexylene, and nitrous oxide. The *hexylene*, probably  $\text{CHBu}\cdot\text{CH}_2$ , is a colourless, mobile, and extremely volatile liquid, resembling light petroleum in odour; it boils at  $67\cdot5$ — $68\cdot5^\circ$  and has a sp. gr. of  $0\cdot683$  at  $15^\circ$ . The corresponding *dibromohehexane*, probably  $\text{CHBuBr}\cdot\text{CH}_2\text{Br}$ , is a colourless liquid, of agreeable ethereal odour, and decomposes when distilled, to some extent even under diminished pressure. It boils at  $90$ — $93^\circ$  (18 mm.); sp. gr. =  $1\cdot604$  at  $15^\circ$ . One of the hexylic alcohols was identified as the normal primary alcohol; the other, which boiled at  $140$ — $142^\circ$ , and had a sp. gr. of  $0\cdot819$  at  $15^\circ$ , yielded a blue pseudonitrole, and was therefore a *secondary alcohol*, probably methylbutylcarbinol. The *dihexylic ether* boiled at  $218$ — $221^\circ$ .

The decomposition, as far as regards the formation of the primary alcohol, resembles that of the nitrites and nitroso-derivatives of the amines, but the mechanism of the formation of the secondary alcohol and the olefine has yet to be explained, for neither of these products can be formed from the other under the conditions under which they are formed from the nitramine. It is possible that the nitramine is simply resolved into the olefine and free nitramide,  $\text{NH}_2\cdot\text{NO}_2$ , and that part of the nitrous oxide is due to the decomposition of the latter.

The monalkylnitramines and those dialkylnitramines, such as diethyl- and dipropyl-nitramine, which do not contain a methyl group, are stable towards alkalis, but the methylalkylnitramines are decomposed by aqueous potash in a complex manner. Dimethylnitramine, for example, yields methylamine, nitrous acid, and formic acid, together with a small amount of dimethylamine, and probably some methylic alcohol. Methylbutylnitramine yields, but with greater difficulty, butylamine and formic and nitrous acids. JN. W.

**Hexamethylenetetramine Salts.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], 13, 352—355).—Hexamethylenetetramine crystallises in forms which belong either to the cubic system or to a closely approximating rhombohedral system; the crystals, which are formed equally well from aqueous and alcoholic solutions, are extremely clear, and highly refractive. The amine is soluble in all the usual solvents with the exception of ether; the percentage solubilities at  $12^\circ$  being  $81\cdot30$  for water,  $3\cdot22$  for alcohol, and  $8\cdot09$  for chloroform.

The *hydrate*,  $\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O}$ , separates in very large striated prisms when the aqueous solution is exposed to temperatures about  $0^\circ$ ; it melts below  $15^\circ$ , but as the quantity of water liberated is insufficient to retain the whole of the amine in solution, a portion of the latter is precipitated in the anhydrous state. The hydrobromide crystallises in brilliant rhombohedra,  $\alpha : \beta : \gamma : \delta = 1 : 1 : 1 : 1\cdot034$ . The *sulphate*,  $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , is a white, crystalline powder, which melts at  $108^\circ$ , boils and probably decomposes at  $130$ — $140^\circ$ , and solidifies and melts again at about  $188^\circ$ ; it is stable at  $100^\circ$ . The *phosphate*,  $5\text{C}_6\text{H}_{12}\text{N}_4\cdot 6\text{H}_3\text{PO}_4 + 10\text{H}_2\text{O}$ , forms white colourless, nacreous crystals, and melts at about  $188^\circ$ , at the same time decomposing. The taste of all three of these salts is extremely acid, and it

is noteworthy that their melting points are all in the neighbourhood of the temperature at which the amine itself decomposes.

JN. W.

**Hexamethylenetetramine Bismuthiodides.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], 13, 351—352).—A fourth *bismuthiodide*,  $(C_6H_{12}N_4 \cdot HI)_2 \cdot (BiI_4H)_3 + 4H_2O$ , is obtained by adding the amine to an excess of the product of the action of acid bismuth sulphate on potassium iodide; it is a dense, orange-yellow microcrystalline precipitate, which, after remaining for several months in contact with the original solution, is transformed into needles of a somewhat redder shade. When heated at  $100^\circ$ , it loses water and becomes still darker in colour, but the dehydrated substance gradually reabsorbs the water on exposure to moist air.

JN. W.

**Action of Methylic Iodide on Dimethylasparagine.** By W. KORNER and ANGELO MENOZZI (*Gazzetta*, 1895, 25, i, 97—100).—The behaviour towards methylic iodide of the dimethylasparagine previously prepared by the authors (*Abstr.*, 1890, 869) is completely analogous to that of asparagine itself; when heated with methylic alcoholic potash and methylic iodide, it yields tetramethylammonium iodide and *methylfumaramic acid*,  $NHMe \cdot CO \cdot CH : CH \cdot COOH$ . The new acid crystallises from water in anhydrous prisms melting at  $208^\circ$ , and yields methylamine and fumaric acid on boiling with aqueous potash; its *potassium* salt separates from water in lustrous, anorthic prisms;  $a : b : c = 0.692 : 1 : 0.441$ .  $\alpha = 85^\circ 32'$ ,  $\beta = 94^\circ 56'$ ,  $\gamma = 73^\circ 19'$ . The *sodium* salt crystallises in transparent laminæ, the *silver* salt is an insoluble, amorphous powder, and the *methylic* salt crystallises in transparent needles melting at  $138^\circ$ .

The acid described by Giustiniani as *methylfumaramic acid* (*Abstr.*, 1892, 821), if pure, cannot have the same constitution as the above, owing to the differences between the melting points and habits.

W. J. P.

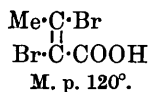
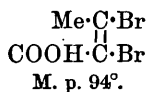
**Glutarimide.** By R. SELDNER (*Amer. Chem. J.*, 1895, 17, 532—535).—Glutarimide,  $CH_2 < \begin{smallmatrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{smallmatrix} > NH$ , is formed by heating together in sealed tubes at  $200$ — $210^\circ$ , glutaric acid (1 mol.) and acetonitrile (2 mols.), or glutaronitrile (1 mol.) and acetic acid (2 mols.), or glutaric acid (1 mol.) and glutaronitrile (1 mol.), a drop or two of acetic anhydride being added to each tube. The last method gives the best yields, in the two others, the glutarimide is mixed with acetic acid and acetonitrile.

C. F. B.

**Addition of Bromine to Tetrolic acid.** By ADOLF PINNER (*Ber.*, 1895, 28, 1877—1887).—The author has previously stated (*Abstr.*, 1881, 793) that tetrolic acid forms a dibromide, which melts at  $95$ — $97^\circ$ . Michael and Pendleton (*Abstr.*, 1888, 1176) have since prepared the same dibromocrotonic acid, and give  $94^\circ$  as the melting point, whilst Fittig and Clutterbuck, by the addition of bromine to tetrolic acid, obtained a dibromocrotonic acid which melted at  $120^\circ$ , but were unable to prepare the acid melting at  $94^\circ$ .

The author has re-examined his acid and finds that it melts at 94°, and not at 95—97° as originally stated; he also finds that his acid is entirely different in crystallographic properties from the acid described by Fittig and Clutterbuck.

It is now shown that the product obtained by the action of bromine on tetrolic acid depends not only on whether the operation is carried out in sunlight or in the dark, but also on the solvent used. Bromine (2 atoms) acts on a cooled aqueous solution of tetrolic acid, forming the dibromocrotonic acid which melts at 120°, together with a small quantity of acraldehyde; if, however, the bromine is added in the dark, the dibromocrotonic acid, of melting point 94°, is formed. Bromine acts in much the same way on tetrolic acid in a chloroform solution cooled to 0°. Even when excess of bromine is employed, one of the dibromocrotonic acids is the product formed, but if carbon tetrachloride is used as the solvent, and the bromination is carried on in direct sunlight, hydrogen bromide is evolved, and the main product is tribromocrotonic acid (m. p. 131°), compare Fittig (*Annalen*, 1892, **268**, 107). When the bromine is added to the carbon tetrachloride solution in the dark, no hydrogen bromide is evolved, and the product is a mixture of the two isomeric dibromocrotonic acids. The author regards these two acids as stereoisomeric.



The acid with the lower melting point is the less stable. Its salts, when heated with water, lose carbonic anhydride and hydrogen bromide, and then form acraldehyde. When hydrogen bromide is passed into a concentrated benzene solution of the acid of lower melting point, it is converted into the isomeric acid of higher melting point.

*Tetrabromocrotonic acid* is obtained when either of the dibrom-acids is dissolved in carbon tetrachloride and treated with bromine in direct sunlight. It crystallises in large, glistening prisms, melts at 146°, and is readily soluble in water or benzene, but only sparingly in carbon tetrachloride, and still more sparingly in light petroleum. The tetrabrom-acid, and also the two dibrom-acids, when treated with sodium amalgam, yield tetrolic acid. If the tetrabrom-acid is neutralised with dilute ammonia, and silver nitrate is added to the solution, decomposition takes place, silver bromide is thrown down, and mucobromic acid,  $\text{COOH} \cdot \text{CBr} : \text{CBr} \cdot \text{CHO}$ , remains in solution.

J. J. S.

**Mixed Anhydrides.** By L. ROUSSET (*Bull. Soc. Chim.*, 1895, [3], 13, 330—334).—The mixed anhydrides of the type  $\text{R} \cdot \text{CO} \cdot \text{O} \cdot \text{CO} \cdot \text{R}'$  do not appear to exist, as their boiling points are indefinite, and they are readily resolved, by fractional distillation, into mixtures, in molecular proportion, of the corresponding simple anhydrides.

Thus the product of the action of acetic chloride on sodium butyrate is a mixture of acetic and butyric anhydrides; Autenrieth's aceto-valeric anhydride, from sodium acetate and valeric chloride, is a mixture of acetic and valeric anhydrides, and the product of the

action of benzoic chloride on sodium acetate is a mixture of acetic and benzoic anhydrides.

The instability of the mixed anhydrides affords a convenient means of preparing anhydrides from acid chlorides. The latter are simply heated with sodium acetate, and the mixtures of anhydrides thus obtained is separated by fractional distillation. JN. W.

**Etherification and Hydrolysis.** By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 1913—1914).—A claim of priority.

**Ozobenzene.** By ADOLPHE RENARD (*Compt. rend.*, 1895, **120**, 1177—1179).—In order to obtain ozobenzene (this Journal, 1873, 610), the benzene must be carefully purified, and the current of ozone must be well dried. When the benzene contains thiophen, only the dark-coloured, non-explosive substance, described by Leeds (*Ber.*, **14**, 975), is formed

Ozobenzene, when freed from excess of benzene by means of a current of dry air, is a white, amorphous substance, which explodes violently on the slightest friction and detonates if heated rapidly to 50°, but decomposes without exploding if very slowly heated. It also detonates in contact with concentrated sulphuric acid, ammonia, or aqueous potash. It remains unchanged in dry air, but decomposes in contact with moist air. In contact with water, it decomposes slowly, with evolution of carbonic anhydride and formation of acetic and formic acids. By weighing the carbonic anhydride evolved, and burning in the usual way the other products of the action of water, it is found that ozobenzene has the composition  $C_6H_6O_6$ . Ozobenzene is insoluble in most organic solvents, but dissolves in acetic acid.

C. H. B.

**Action of Acid Chlorides on  $\alpha$ -Hexachlorophenol in Presence of Aluminium Chloride.** By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], **13**, 340—345).—When aluminium chloride is added to a cooled carbon bisulphide solution containing  $\alpha$ -hexachlorophenol and an acid chloride, there is a slight elevation of temperature, but no evolution of hydrogen chloride, and crystals of an additive metallic compound can be separated from the product (see following abstract); at a higher temperature, however (35—40°), a violent action takes place, hydrogen chloride is evolved, and a nearly quantitative yield of crystals of the acidyl derivative of pentachlorophenol is obtained. The crystalline product, after being drained, is digested with cold water to decompose the sulphur chloride formed in the action, and the dry substance is recrystallised from benzene or light petroleum.

*Pentachlorophenylic acetate*,  $C_6Cl_5 \cdot OAc$ , crystallises in long, slender, monoclinic prisms, and melts at 149.5—150.5°, not at 148—149° as stated by Weber and Wolff; it remains practically unaffected by boiling with concentrated aqueous potash, but is completely hydrolysed by alcoholic potash at 120°. The *propionate* forms long, soft, white, silky needles, and melts at 78.5°. It is easily hydrolysed by alkalis. The *butyrate* separates from light petroleum as a felted mass of fine, white, soft needles; it softens at 49° and melts at 59—62.5°, but the product obtained was not quite pure, as the compound is

hydrolysed, even by moist air, into its proximate constituents. The benzoate crystallises in colourless, highly refractive, monoclinic prisms, sp. gr. = 1.711 at 18°, and melts at 159—160°. It is stable towards strong, boiling, aqueous potash, but is hydrolysed by alcoholic potash at 120°.

It is probable that the sulphur chloride and the carbon sulphochloride formed in the preparation result from the action of nascent chlorine on the carbon bisulphide, this chlorine being produced, together with the compound  $\text{C}_6\text{Cl}_5\cdot\text{O}\cdot\text{Al}_2\text{Cl}_6$ , by the decomposition of the original additive compound. JN. W.

**Action of Aluminium Chloride on  $\alpha$ -Hexachlorophenol.** By ETIENNE BARRAL (*Bull. Soc. Chim.* 1895, [3], 13, 345—348).—When  $\alpha$ -hexachlorophenol is heated with aluminium chloride ( $\frac{1}{8}$  mol.) in sealed tubes at 160—165°, the chief products are pentachlorophenol and chloranil. With more of the chloride ( $\frac{1}{2}$  mol.), and at 170—175°, much carbonyl chloride is formed, and the principal product is hexachlorobenzene, whilst with the same proportion of the chloride, and in presence of carbon bisulphide, a reaction occurs similar to that described in the preceding abstract, pentachlorophenol, sulphur chloride, and carbon sulphochloride being formed; at a higher temperature, however, a small quantity of *pentachlorophenylic carbonate*,  $\text{CO}(\text{O}\cdot\text{C}_6\text{Cl}_5)_2$ , is produced. This forms very small, colourless, nacreous crystals, which begin to sublime at about 250° and melt at 265—268°; it can be volatilised without decomposing. JN. W.

**Preparation of Orthodibromaniline.** By W. KORNER (*Gazzetta*, 1895, 25, i, 95—97).—Orthodibromaniline [ $\text{NH}_2 : \text{Br}_2 = 1 : 3 : 4$ ] is readily prepared by acetylating metabromaniline with acetic anhydride and brominating the resulting metabromacetanilide in acetic acid solution; it melts at 80.4—80.5°, and gives crystalline salts. The *monacetyl* derivative,  $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NHAc}$ , crystallises in thin prisms melting at 128°, and the *diacetyl* derivative,  $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NAc}_2$ , forms lustrous scales, melting and decomposing at 208°. This dibromaniline is violently acted on when warmed with alcoholic ethylic nitrite, nitrogen being evolved and orthodibromobenzene being produced. W. J. P.

**Conversion of an Aniline Salt into an Anilic acid.** By LOUIS SIMON (*Compt. rend.*, 1895, 120, 1174—1177).—Pyruvic acid and aniline do not form aniline pyruvate, but only *anilpyruvic acid*, which seems to be a consequence of the presence of the ketonic function. On the other hand, phenylglyoxylic acid yields exclusively the ordinary salt. It would seem, however, that this difference is more apparent than real, for, although aniline phenylglyoxylate when heated loses carbonic anhydride and water and is converted into benzyldeneaniline,  $\text{CHPh}\cdot\text{NPh}$ , when dissolved in cold methylic alcohol, or when boiled with chloroform or benzene, it is completely converted into *anilphenylglyoxylic acid*,  $\text{NPh}\cdot\text{CPh}\cdot\text{COOH}$ , a white, crystallisable compound, melting and decomposing at 151° with formation of the compound  $\text{CHPh}\cdot\text{NPh}$ . Anilphenylglyoxylic acid

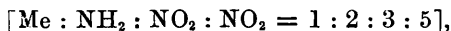


is insoluble in boiling benzene or chloroform, and only slightly soluble in ether or cold acetic acid. When boiled with water, it is completely reconverted into aniline phenylglyoxylate. It also dissolves in acids and alkalis. Aniline phenylglyoxylate yields an abundant precipitate with phenylhydrazine, but anilphenylglyoxylic acid does not, and this is a further proof that the ketonic function existing in the one is non-existent in the other.

Ammonia and the toluidines yield similar results. C. H. B.

**Benzenesulpho-orthotoluidide and its Derivatives.** By CH. RABAUT (*Compt. rend.*, 1895, **120**, 1123—1126).—*Benzenesulpho-orthotoluidide*,  $C_6H_5SO_2NH \cdot C_6H_4Me$ , is obtained by heating benzenesulphonic chloride (1 mol.) with orthotoluidine (2 mols.), in presence of benzene or strong alcohol. It separates from alcohol in white crystals, which melt at 122—123°, and boil without decomposing at about 290—295° under a pressure of 50 to 60 mm. It is insoluble in water, but dissolves in alkalis and organic solvents. When boiled with nitric acid of sp. gr. 1.10, it yields a yellow dinitro-derivative,  $SO_2Ph \cdot NH \cdot C_6H_4Me(NO_2)_2$ , which melts at 167—168°. Under similar conditions acetylorthotoluidine is completely decomposed into acetic acid and toluidine.

The dinitro-derivative, when heated in sealed tubes at 140° with concentrated hydrochloric acid, yields a dinitrotoluidine,



which melts at 208—209°, and was described by Städel (*Abstr.*, 1881, 724). When treated by Prud'homme and Rabaut's method (*Abstr.*, 1892, 705), it yields the chloride  $C_6H_4Me(NO_2)_2Cl$  [ $Me : Cl : NO_2 : NO_2 = 1 : 2 : 3 : 5$ ], which forms yellow crystals melting at 45—46°.

It follows that the original dinitro-derivative has the constitution  $[Me : NO_2 : NO_2 : NH \cdot SO_2 = 1 : 3 : 5 : 6]$ , the two benzene nuclei being linked by the group  $SO_2NH$ . It has strongly marked acid properties, dissolves in alkalis, and decomposes barium carbonate at 100°, forming a barium salt which separates in yellow crystals; these lose 1 mol.  $H_2O$  at 140°, and only decompose at about 215°. Hydrochloric acid precipitates the dinitro-derivative, which can thus be purified. Reduction with tin and hydrochloric acid yields the diamine in white needles, which melt at 217° and turn red when exposed to air. It forms salts very soluble in water, and is readily diazotised.

The general stability of benzenesulpho-orthotoluidide, notwithstanding its amide character, is especially noteworthy.

C. H. B.

**Reduction by means of Phenylhydrazine.** By R. WALTHER (*J. pr. Chem.*, 1895, [2], 141—144).—The author draws attention to the application of phenylhydrazine as a reducing agent in organic chemistry; such reductions as that of azobenzene to hydrazobenzene, and that of nitro-compounds to the corresponding amido-derivatives being easily effected by its means.

A. G. B.

**Isohydroxydiphenylethylamine from Glycocine and Benzaldehyde.** By EMIL ERLÉNMEYER, Jun. (*Ber.*, 1895, **28**, 1866—1869).—The author has previously shown (*Abstr.*, 1893, i, 166) that benzaldehyde and glycocine, in dilute alcoholic solution and in presence of sodium hydroxide, condense to form a sodium salt,

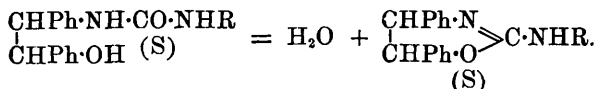


and a substance soluble in alcohol. The latter has since been investigated, and is now shown to have the composition



When treated with hydrochloric acid, it is decomposed into benzaldehyde and *isohydroxydiphenylethylamine*; this base, which melts at 128°, stands in the same relation to the diphenylhydroxyethylamine (m. p. 161°) of Goldschmidt and Polonowska (*Abstr.*, 1887, 492) as isohydrobenzoin does to hydrobenzoin. If distilled with zinc dust, it yields stilbene; when oxidised, it gives benzile, and when diazotised and converted into the corresponding glycol, it yields isohydrobenzoin; if heated to about 130°, it decomposes into benzaldehyde and benzylamine. The original condensation product can be regenerated by heating isodiphenylhydroxyethylamine with benzaldehyde in alcoholic solution. The author regards his base and isohydrobenzoin as the true analogues of racemic acid, on account of the hemimorphic character of their crystals; whereas hydroxydiphenylethylamine and hydrobenzoin are the analogues of mesotartaric acid. J. J. S.

**Heterocyclic Bases from Hydroxydiphenylethylamine.** By HENRYK G. SÖDERBAUM (*Ber.*, 1895, **28**, 1897—1903).—The carbamide and thiocarbamide derivatives obtained by treating hydroxydiphenylethylamine respectively with isocyanates and thiocarbimides readily yield condensation products according to the scheme



These condensation products are strongly basic, forming salts which are not decomposed by water; they also yield crystalline platinochlorides, which are for the most part sparingly soluble. They greatly resemble the amidobenzoxazoles (amidobenzothiazoles), but are totally different from the isomeric  $\beta$ -oximidazoles, and are to be

regarded as derivatives of the compound  $\begin{array}{c} \text{CH}_2\cdot\text{N} \\ \text{CH}_2\cdot\text{O} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}\cdot\text{NH}_2$ , which the

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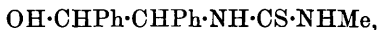
author terms *dihydroamidoazoxole* (*dihydroamidoazthiole*).

*Hydroxydiphenylethylcarbamide*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , is obtained from hydroxydiphenylethylamine hydrochloride and potassium cyanate in aqueous solution. It forms colourless crystals, melts at 215°, and is insoluble in water and ether, but dissolves in acetone and hot alcohol.

4:5-Diphenyldihydro-2-amido-1:3-azoxole is obtained when the preceding compound is heated with dilute hydrochloric acid for

1—2 hours, and the solution precipitated with sodium hydroxide. It crystallises in six-sided needles, and melts at 153—154°. The platinumchloride,  $(C_{15}H_{14}N_2O)_2, H_2PtCl_6$ , forms minute, yellowish crystals, and melts at 203°.

*Methylhydroxydiphenylethylthiocarbamide,*

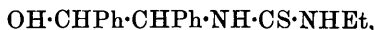


obtained from hydroxydiphenylethylamine and methylthiocarbimide, forms colourless plates which melt at 136°.

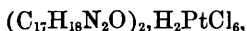
4 : 5-Diphenyldihydro-2-methylamido-1 : 3-azoxole is obtained by treating the preceding compound in alcoholic solution with yellow mercuric oxide; it forms colourless, glistening needles, and melts at 158—159°. The platinumchloride,  $(C_{16}H_{16}N_2O)_2, H_2PtCl_6$ , crystallises in minute, yellowish plates which decompose at 215°.

4 : 5-Diphenyldihydro-2-methylamido-1 : 3-azothiole, when recrystallised from alcohol, forms large, colourless prisms, and melts at 155°. The platinumchloride  $(C_{16}H_{16}N_2S)_2, H_2PtCl_6$ , crystallises in yellowish-red prisms which undergo decomposition at 220°.

*Ethylhydroxydiphenylethylthiocarbamide,*

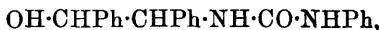


crystallises in small needles, and melts at 148—149°. When treated with mercuric oxide, it yields 4 : 5-Diphenyldihydro-2-ethylamido-1 : 3-azoxole, which melts at 141°; its platinumchloride,



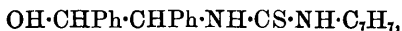
crystallises in yellowish prisms, and melts at 195—200°. The corresponding azothiole,  $C_{17}H_{16}N_2S$ , melts at 139°, and forms a platinumchloride which melts at 185—188°.

*Phenylhydroxydiphenylethylthiocarbamide,*



prepared from hydroxydiphenylethylamine and phenylthiocarbimide, forms colourless crystals, and melts at 176°; the corresponding phenylhydroxydiphenylethylthiocarbamide melts at 171°, and when treated with mercuric oxide yields 4 : 5-diphenyldihydro-2-phenylamido-1 : 3-azoxole, which crystallises in small, white needles and melts at 162—163°; its platinumchloride,  $(C_{21}H_{16}N_2O)_2, H_2PtCl_6 + 3H_2O$  forms yellow, glistening needles, which undergo decomposition at 195—198°.

*Orthotolylhydroxydiphenylethylthiocarbamide,*



crystallises from toluene in short, white needles, which melt at 156—157°. When treated with mercuric oxide, it gives 4 : 5-diphenyldihydro-2-orthotolylamido-1 : 3-azoxole, which melts at 136—138°; its platinumchloride,  $(C_{22}H_{20}N_2O)_2, H_2PtCl_6$ , melts at 220—225°.

J. J. S.

**Aromatic Nitroso-bases.** By OTTO FISCHER (*Annalen*, 1895, 286, 145—186).—In a short introduction, the author discusses the constitution of aromatic nitroso-bases.

By OTTO FISCHER and E. SCHÄFFER.—The *hydrochloride* of *para-nitrosoaniline*,  $C_6H_5N_2O.HCl$ , separates from alcohol in dark brown crystals; the *sulphate* crystallises in yellowish-white prisms. The *oxalate* forms small, greenish crystals, and the *picrate* separates as a brown mass of crystals on adding ether to the alcoholic solution. The *dibenzoyl* derivative crystallises in dark brown needles or leaflets, and melts at  $142^\circ$ ; in preparing it, it is necessary to dissolve the nitrosoaniline in a dilute solution of sodium hydroxide and agitate the cold liquid with excess of benzoic chloride; otherwise, if strong soda is used and the mixture is allowed to get warm, benzoylnitrosophenol is formed. *Orthohydroxybenzylideneparanitrosoaniline* is prepared by heating the base with salicylaldehyde for two hours at  $100^\circ$ ; it softens at  $235^\circ$ , and melts at  $245^\circ$ . Paranitraniline is formed when paranitrosoaniline is oxidised with potassium permanganate, whilst reducing agents give rise to paraphenylenediamine.

By OTTO FISCHER and H. APITSCH.—The *picrate* of *paranitrosoethylaniline* crystallises from water in dark yellow needles, and melts at  $131^\circ$ ; the *silver* salt, which has the composition  $3C_8H_{10}N_2O.AgNO_3$ , separates in small, dark green, lustrous crystals, and melts and decomposes at  $121^\circ$ . The *mercurochloride* melts and decomposes at  $142^\circ$ .

The nitrosamine of paranitrosoethylaniline is very stable in presence of reducing agents. With acetic acid and zinc-dust, a colourless oil is obtained, which gives Liebermann's reaction; on adding sodium amalgam to the cold alcoholic solution of the nitrosamine, the liquid becomes reddish-brown, and a yellow precipitate is formed, which, when recrystallised from alcohol, melts at  $171^\circ$ . This compound has the formula  $C_{16}H_{18}N_6O_3$ , and gives Liebermann's reaction; on reduction, it yields ethylparaphenylenediamine.

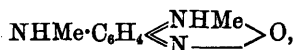
$\alpha$ -Nitroso- $\alpha$ -methylnaphthylamine,  $C_{10}H_8 \llcorner \begin{smallmatrix} NMe \\ N \end{smallmatrix} > O$ , is prepared by dissolving  $\alpha$ -methylnaphthylamine in dilute sulphuric acid, adding sodium nitrite, and extracting with ether; the nitrosamine, which is left as a viscid oil on evaporation of the ether, is converted into the *hydrochloride* of nitrosomethylnaphthylamine by treatment with alcoholic hydrochloric acid; this salt crystallises in slender, pale green needles; the *picrate* crystallises in greenish-yellow needles, and melts and decomposes at  $157^\circ$ . Nitrosomethylnaphthylamine gives the indazine reaction, a blue colouring matter being produced on treating the alcoholic solution of the hydrochloride with diphenylmetaphenylenediamine; this product, symmetrical *anilido-n-methylrosinduline*,  $NMe.C_{10}H_7 \llcorner \begin{smallmatrix} N \\ NPh \end{smallmatrix} > C_6H_5.NHPh$ , forms magnificent, golden-green crystals, and melts and decomposes at  $225^\circ$ . The *hydrochloride* was analysed.

When salicylaldehyde is heated with  $\alpha$ -nitroso- $\beta$ -naphthylamine for 2—3 hours on the water bath, a compound,  $C_{17}H_{12}N_2O_2$ , is obtained, which separates from alcohol in green leaflets, and melts at  $270^\circ$  on treating it with boiling acids, salicylaldehyde is formed.

By OTTO FISCHER and EMIL DIEPOLDER.—*Orthonitrobenzylidene-orthoparatolylenediamine*,  $NHEt.C_6H_3Me.N:CH.C_6H_4.NO_2$ , is obtained

by condensation of monethylorthoparatolylenediamine with ortho-nitrobenzaldehyde; it crystallises in lustrous, reddish-brown leaflets, and melts at  $80^{\circ}$ . The *metanitro*-derivative crystallises in yellow needles, and melts at  $118^{\circ}$ ; the *paranitro*-derivative crystallises from alcohol in long, red needles, and melts at  $143^{\circ}$ . The *orthohydroxy*-derivative crystallises from light petroleum in nodular aggregates of yellow prisms, and melts at  $62^{\circ}$ . The *thiocarbamide*,  $C_{19}H_{26}N_4S$ , obtained by boiling carbon bisulphide and a small quantity of alcohol with monethylorthoparatolylenediamine, crystallises from alcohol in small, white needles and melts at  $163^{\circ}$ . The *benzoyl* derivative of monethylorthoparatolylenediamine crystallises from light petroleum in small needles, and melts at  $174^{\circ}$ .

The *acetyl* derivative of trimethylmetaphenylenediamine is obtained by heating a solution of acetyldimethylmetaphenylenediamine in xylene with sodium, and, when the metal is dissolved, heating the liquid with methylic iodide; it separates from alcohol in large crystals, and melts at  $68^{\circ}$ . The *base* boils at  $270^{\circ}$ , and when its solution, in 10 per cent. sulphuric acid, cooled with ice, is treated with sodium nitrite in dilute aqueous solution, the liquid becomes deep red, and the *dinitrosamine* of dimethylmetaphenylenediamine is precipitated; this crystallises from alcohol in lustrous, brown leaflets, and melts at  $109$ – $110^{\circ}$ . The quantity of this substance amounts to 5 per cent. of the trimethyl derivative employed, and on extracting the liquor from which it separates with boiling ether, the *nitrosamine* of trimethylmetaphenylenediamine is obtained; the *hydrochloride* crystallises in colourless leaflets, and on treating it with boiling methylic or ethylic alcohol, a deep red liquid is obtained, and the *monhydrochloride* of *paranitrosotrimethylmetaphenylenediamine* separates in dark red crystals with green lustre. The *dihydrochloride* crystallises in dark red needles. The base itself, *paranitrosodimethylmetaphenylenediamine*,  $NMe \cdot C_6H_4 \cdot \left\langle \begin{smallmatrix} N \\ \text{---} \end{smallmatrix} \right\rangle O$ , crystallises from benzene in long, steel-blue prisms, which appear red by transmitted light, and contain the solvent; it melts at  $143^{\circ}$ . On adding aqueous sodium nitrite to a solution of the base in dilute sulphuric acid, a *nitro*-derivative of trimethylmetaphenylenediamine nitrosamine is formed, crystallising from ether in yellow needles, and melting at  $157^{\circ}$ . *Paranitrosodimethylmetaphenylenediamine*,



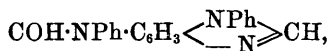
is another product of the action of nitrous acid on trimethylmetaphenylenediamine; after removing the dinitrosamine of dimethylmetaphenylenediamine, the liquid is treated with excess of potassium carbonate, rapidly extracted with ether to remove unaltered trimethylmetaphenylenediamine, and then allowed to remain at the ordinary temperature for 24 hours, the base separating in quantity amounting to 40 per cent. of the substance employed. It crystallises from benzene in steel-blue needles containing the solvent; the *sulphate* crystallises from water in red needles. On reducing to a small bulk the liquid from which the base has been removed, para-

nitrosotrimethylmetaphenylenediamine is obtained: the action of nitrous acid on trimethylmetaphenylenediamine, therefore, gives rise to four products, the nitrosamine of trimethylmetaphenylenediamine, the dinitrosamine of dimethylmetaphenylenediamine, paranitrosotrimethylmetaphenylenediamine, and paranitrosodimethylmetaphenylenediamine.

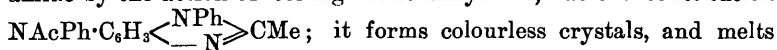
Symmetrical *dimethylmetaphenylenediamine* is obtained by heating the formyl derivative of monomethylphenylenediamine with sodium methoxide and methylic iodide, and hydrolysing the product with dilute sulphuric acid. It is a colourless oil which, however, rapidly becomes brown; it boils at 165–170° under a pressure of 10 mm., and at 275–280° under a pressure of 739 mm. The dinitrosamine (m. p. 109–110°) is identical with the product of the action of nitrous acid on trimethylmetaphenylenediamine; when it is dissolved in ether, and treated with cold, alcoholic hydrogen chloride, symmetrical *paranitrosodimethylmetaphenylenediamine* is obtained in the form of the hydrochloride. This base separates from ether in magnificent, steel-blue crystals, and melts at 171°.

BY OTTO FISCHER AND M. GMELIN.—Paranitrosodiphenylmetaphenylenediamine melts at 153°. When an alcoholic solution of the hydrochloride is heated with aqueous phenylhydrazine hydrochloride at 50–60°, a compound,  $C_{24}H_{21}N_5$ , is formed, which separates from alcohol in pale rose-coloured crystals, and melts at 160°; it is almost insoluble in acids and alkalis, and, when mixed with cupric oxide and heated suddenly, it decomposes explosively.

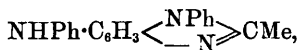
*Formylanilido-n-phenylmethenylphenylenediamine*,



is obtained by heating amidodiphenylmetaphenylenediamine (the reduction product of paranitrosodiphenylmetaphenylenediamine) with concentrated formic acid for several hours; it crystallises from hot, dilute alcohol in colourless needles, and melts at 124°. The *acetylanhydro-base*, obtained from amidodiphenylmetaphenylenediamine by the action of boiling acetic anhydride, has the constitution



it forms colourless crystals, and melts at 165°. *Anilido-n-phenylethenylphenylenediamine*,



is obtained by treating the foregoing compound with boiling dilute sulphuric acid; it crystallises in large, colourless plates melting at 115°, and the *sulphate* crystallises in white leaflets.

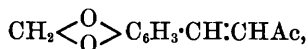
When amidodiphenylmetaphenylenediamine is heated on the water bath with salicylaldehyde, a *hydroxybenzylidene* derivative is formed, which crystallises in dark yellow prisms; on recrystallising this substance two or three times from absolute alcohol containing benzene, *anilido-n-phenylortho-hydroxybenzenylphenylenediamine* is obtained, crystallising in pale yellow needles, and melting at 190°. The *ortho-benzylidene* derivative is brown, being converted into the *anhydro-*

base on recrystallising it from alcohol; this crystallises in orange needles, and melts at  $210^{\circ}$ . When amidodiphenylmetaphenylenediamine is heated with carbon bisulphide and alcohol for four hours in a reflux apparatus, the compound  $\text{NHPh}\cdot\text{C}_6\text{H}_5\cdot\text{N}(\text{Ph})\text{C}\cdot\text{SH}$  is formed; it crystallises from absolute alcohol in yellow needles, and melts at  $208^{\circ}$ . The sodium salt separates from the alkaline solution in white leaflets, and is decomposed by water.

By OTTO FISCHER AND W. HOFMANN.—The *acetyl* derivative of paranitrosophenyl- $\alpha$ -naphthylamine crystallises from wood spirit in lustrous, reddish-yellow leaflets, and melts at  $81^{\circ}$ . On reducing the base with zinc dust and acetic acid, paramidophenyl- $\alpha$ -naphthylamine is formed; the *acetyl* derivative crystallises in white leaflets, and melts at  $192^{\circ}$ , the *benzylidene* compound,  $\text{NHPh}\cdot\text{C}_{10}\text{H}_7\cdot\text{N}\cdot\text{CHPh}$ , separates from absolute alcohol in greenish-yellow crystals, and melts at  $109^{\circ}$ ; and the *orthohydroxybenzylidene* derivative crystallises in long, red needles, and melts at  $135^{\circ}$ . The *metanitrobenzylidene* compound crystallises in red leaflets, melting at  $169^{\circ}$ , and the *para-nitrobenzylidene* derivative crystallises in very dark red leaflets, and melts at  $168^{\circ}$ ; the *thiocarbamide*,  $\text{CS}(\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\text{NHPh})_2$ , forms white crystals, and melts at  $196^{\circ}$ .

$\alpha$ -Naphthaquinonephenyldiimide,  $\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NPh}$ , is obtained by agitating a solution of amidophenyl- $\alpha$ -naphthylamine in benzene with mercuric oxide; it forms lustrous, reddish-yellow crystals, and melts at  $128$ — $129^{\circ}$ .  
M. O. F.

**Piperonylideneacetone.** By L. ROUSSET (*Bull. Soc. Chim.*, 1895, [3], 13, 348—351).—*Piperonylideneacetone*,



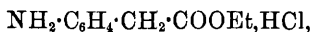
is formed as a yellow precipitate when a solution of piperonal in acetone is shaken with a large excess of cold, 10 per cent., aqueous soda; when purified by recrystallisation from alcohol, it forms minute, yellow, prismatic needles, belonging either to the monoclinic or to the triclinic system, but the product obtained by distillation with steam is colourless; it melts at  $96.5^{\circ}$ .

The *oxime* is colourless, and melts at about  $179^{\circ}$ , at the same time decomposing. The *dibromo*-derivative forms colourless crystals, and melts at  $76^{\circ}$ ; it decomposes at  $100^{\circ}$ .

Piperonylideneacetone is oxidised by chromic acid mixture to piperonylic and acetic acids, and carbonic anhydride. JN. W.

**Reducing Action of Sodium Alkyl Oxides at High Temperatures.** By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1895, 120, 1105—1106).—Phenyl benzyl ketone, when heated in sealed tubes at  $200$ — $210^{\circ}$  with sodium ethoxide in presence of excess of alcohol, yields stilbene. Diphenyl ketone, under similar conditions, yields benzhydrol. Anthraquinone, with sodium ethoxide, butyloxide, or amyloxide, yields anthracene. Methyl phenyl ketone seems to yield phenylmethylcarbinol.  
C. H. B.

**Ethereal Salts of Amido-acids.** By HEINRICH SALKOWSKI (*Ber.*, 1895, **28**, 1917—1923).—When an attempt is made to crystallise the hydrochloride of paramidophenylacetic acid from boiling alcohol, it is converted into the *hydrochloride* of its *ethylic salt*,



which separates in plates, and, on treatment with cold soda solution, yields *ethylic paramidophenylacetate*, melting at 49.5°. The formation of the ethylic salt does not take place at the ordinary temperature, but a similar action occurs on boiling the hydrochloride of the acid with methylic, normal propylic, or amylic alcohol, although, in the case of the first named, the action is far from complete. The hydrochloride of metamidophenylacetic acid behaves in the same manner.

In order to ascertain whether this property is characteristic of aromatic amido-acids in general, the author has examined the behaviour of a number of these, and finds that the hydrochlorides of ortho-, meta-, and paramidobenzoic acids undergo no etherification under these conditions, but that the amidocinnamic and amidohydrocinnamic acids all readily undergo etherification; the results are not altered if the hydrobromide, hydriodide, or nitrate are employed in place of the hydrochloride, but with the sulphate no etherification takes place. It appears, therefore, that aromatic amido-acids in which the carboxyl group is not directly combined with the benzene nucleus undergo etherification by the action of boiling alcohol on their salts with hydrochloric, hydrobromic, hydriodic, or nitric acid, the relative position of the amido-group to the side chain containing the carboxyl having no influence. This conclusion is analogous in many respects to that of V. Meyer and Sudborough (*Abstr.*, 1894, i, 463), who have shown that diortho-substituted benzoic acids do not undergo etherification when treated with methylic alcohol and hydrochloric acid, but that etherification readily takes place in diortho-substituted acids with longer side chains.

H. G. C.

**Action of Hydrazine Hydrate on Benzylidenecyanhydrin.** By ATTILIO PURGOTTI (*Gazzetta*, 1895, **25**, i, 117—121).—On boiling an alcoholic solution of benzylidenecyanhydrin with hydrazine hydrate and distilling off the alcohol, a residue is obtained from which a small proportion of  $\alpha$ -toluonitrile may be separated by fractional distillation; no other product was isolated.

W. J. P.

**Preparation of Thymolphthalide.** By PIOTR JAKIMOWICZ (*Ber.*, 1895, **28**, 1876).—The author has obtained thymolphthalide,  $\text{C}_6\text{H}_4 < \text{C} \begin{smallmatrix} \text{CO} \\ \text{OC}(\text{C}_{10}\text{H}_{13})_2 \end{smallmatrix} > \text{O}$ , by gently warming powdered thymol (2 mols.) with phthalic chloride (1 mol.). It crystallises in thick, colourless plates, melts at 84—85°, and dissolves in concentrated sulphuric acid, forming a dark red solution.

J. J. S.

**Methylic Carbonates derived from Polyhydric Phenols.** By VICTOR SYNIEWSKI (*Ber.*, 1895, **28**, 1874—1876).—If quinol (1 mol.) intimately mixed with calcined sodium carbonate, is added to a solu-



tion of methylic chloroformate in benzene, and the mixture heated during several hours on the water bath, *methylic quinol dicarbonate*,  $C_6H_4(O\cdot COOMe)_2$ , is formed; this crystallises in long, thin, colourless plates, which melt at  $115^\circ$ .

*Methylic resorcinol dicarbonate* forms long, white needles, and melts at  $44-45^\circ$ .

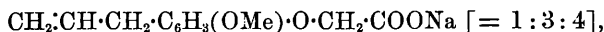
In preparing the corresponding catechol and pyrogallol derivatives, calcium carbonate must be substituted for the sodium carbonate.

*Methylic catechol dicarbonate* crystallises in fine, colourless needles, and melts at  $41^\circ$ .

*Methylic pyrogallol tricarbate*,  $C_6H_3(O\cdot COOMe)_3$ , is a thick, yellowish oil.

*Methylic orcinol dicarbonate*,  $C_6H_3Me(O\cdot COOMe)_2$ , forms long, colourless needles, and melts at  $55^\circ$ . J. J. S.

**Eugenol Derivatives.** By CH. GASSMANN and EUGEN KRAFFT (*Ber.*, 1895, 28, 1870—1872).—*Sodium eugenolacetate*,



is obtained when eugenol is heated with sodium hydroxide solution and monochloroacetic acid during 20 hours. The acid crystallises in colourless needles, melts at  $75^\circ$ , and is readily soluble in hot water, alcohol, acetone, benzene, and light petroleum, but only sparingly in cold water; it is only slightly volatile with steam. When this acid is heated with potassium hydroxide and amyl alcohol during 20 hours, it is converted into *potassium isoeugenolacetate*. *Isoeugenolacetic acid* forms colourless needles, and melts at  $92-94^\circ$ ; it cannot be crystallised from water.

When the iso-acid is oxidised with potassium permanganate in alkaline, or, better still, in neutral, solution, the chief products are acetaldehyde and *vanillinacetic acid*,



which is identical with the acid described by Elkan (*Abstr.*, 1887, 259) as vanillinaxyacetic acid. When the acid is treated with phosphorus pentachloride (2 mols.), vanillin, trichloroacetic acid, and carbonic anhydride are formed. J. J. S.

**Phenylazocarboxylic acid and Tribromophenylazocarboxylic acid.** By OSCAR WIDMAN (*Ber.*, 1895, 28, 1925—1931).—E. Fischer has shown (*Abstr.*, 1878, 302) that when phenylsemicarbazide is treated with sodium nitrite in acid solution, it yields a crystalline nitroso-derivative, and that this, on boiling with alkalis, is converted into diazobenzeneimide, carbonic anhydride, and water. The author has reinvestigated this substance, which has the constitution,  $NO\cdot NPh\cdot NH\cdot CO\cdot NH_2$ , and melts at  $126-127^\circ$ , with evolution of nitrous fumes. If kept for a long time, it undergoes spontaneous decomposition into *phenylazocarbamide*,  $NPh\cdot N\cdot CO\cdot NH_2$ , which may, however, be more readily obtained by carefully oxidising phenylsemicarbazide with potassium permanganate or dichromate. It crystallises from water or benzene in long, red needles, melting at  $114^\circ$ ,

does not reduce Fehling's solution, but evolves nitrogen on the addition of copper powder to the boiling aqueous solution; it evolves ammonia on warming in alkaline solution, and forms salts of phenylazocarboxylic acid, which are yellow, but have not been obtained pure; on the addition of acids, it decomposes, forming benzene, carbonic anhydride, and nitrogen, together with other products.

*Ethyl phenylcarbazinate*,  $\text{NPh}\cdot\text{NH}\cdot\text{COOEt}$ , obtained by mixing phenylhydrazine and ethylic chloroformate in ethereal solution, crystallises in long plates, or flat needles; these contain 1 mol.  $\text{H}_2\text{O}$ , which is evolved on heating at  $85^\circ$ ; the hydrated compound melts at  $79\text{--}80^\circ$ , and the anhydrous compound at  $82\text{--}83^\circ$ . The solution in concentrated sulphuric acid is coloured deep red by ferric chloride. When oxidised by potassium permanganate, it yields ethylic phenylazocarboxylate,  $\text{NPh}\cdot\text{N}\cdot\text{COOEt}$ , which is a thin, red oil, and is converted into phenylazocarbamide on treatment with concentrated ammonia.

These substances are closely allied to the azodicarbamide derivatives obtained by Thiele (Abstr., 1892, 1429), the additive compounds of diazocyanides and hydrocyanic acid obtained by Gabriel (Abstr., 1880, 41), and further with the substituted diazocyanides recently described by Hantzsch and Schultze (this vol., i, 348) which exist in two modifications, regarded by them as stereoisomerides. Theoretically, the above derivatives are also capable of existing in two stereoisomeric forms, and the author has endeavoured to obtain evidence on this point, employing symmetrical tribromophenylsemicarbazide as the starting point, as this forms more stable derivatives.

Symmetrical *tribromophenylsemicarbazide*,



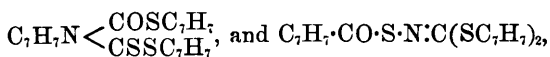
is readily obtained by the action of potassium cyanate and acetic acid on symmetrical tribromophenylhydrazine, and forms very sparingly soluble needles, melting at  $235\text{--}236^\circ$ , with evolution of gas. When oxidised with acetic acid and potassium permanganate, it is converted into the corresponding symmetrical *tribromophenylazocarbamide*,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises from benzene in long, flat, red needles, and melts and evolves gas at  $176^\circ$ ; no definite evidence of the existence of an isomeric compound could, however, be obtained.

*Potassium tribromophenylcarboxylate* may be obtained by the action of aqueous potash on the carbamide; it crystallises in long, yellow needles, which explode on warming, or when touched with concentrated sulphuric acid. On adding dilute sulphuric acid to the well cooled solution, a yellowish-white precipitate separates, probably consisting of the free tribromophenylazocarboxylic acid, but this decomposes in a few seconds with evolution of gas and formation of tribromobenzene.

During the investigation, the following acetyl derivatives of symmetrical tribromophenylhydrazine were prepared.  $\beta$ -*Acetyltribromophenylhydrazine*,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}\cdot\text{NHAc}$ , which forms well developed, four-sided prisms, and melts at  $188^\circ$ , and  $\alpha\beta$ -*diacetyltribromophenylhydrazine*,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}\cdot\text{NAc}_2$ , crystallising in brittle needles melting at  $144\text{--}145^\circ$ .

H. G. C.

**Sulphur Derivatives of Imidodicarboxylic acid.** By EMIL FROMM (*Ber.*, 1895, **28**, 1935—1940).—The imidodicarboxylates described by the author (*Abstr.*, 1893, i, 575, this vol., i, 418, 461), are, with one exception, not acted on by alkyl haloids in alkaline solution with substitution of the alkyl radicle for the hydrogen of the imidogroup. Trithiodibenzylid imidodicarboxylate, however, is acted on under these conditions forming *trithiotribenzylid pseudoimidodicarboxylate*, which crystallises in spherical aggregates of needles melting at 92°. Two formulæ are possible for this substance, namely,



as, however, it yields no benzylamine, but considerable quantities of ammonia when distilled with aqueous potash, its constitution must be represented by the second formula. In its formation, the trithiodibenzylid imidodicarboxylate reacts in the tautomeric form,



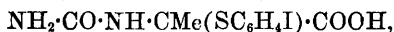
and it is probably owing to their incapability of reacting in this form that the other imidodicarboxylates are not affected by benzylic chloride and soda.

When phenylmethylthiobiuret is heated with benzylic mercaptan and hydrochloric acid on the water bath, it is converted into *benzylic trithioallophanate*,  $\text{C}_7\text{H}_7\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , which forms sulphur-yellow needles and melts at 142—143°. The action of ammonia on this substance was investigated in the hope that the hitherto unknown dithiobiuret would be formed; this is, however, not the case, the products of the action being benzylic mercaptan and ammonium thiocyanate.

H. G. C.

**Pariodophenylmercapturic acid.** By EUGEN BAUMANN and P. SCHMITZ (*Zeit. physiol. Chem.*, 1895, **20**, 586—594).—The acid was obtained from the urine of a dog to which iodobenzene (100 grams) had been administered during about six weeks; the yield was 20—21 per cent. of the iodobenzene employed. The compound crystallises in aggregates of long needles, melts at 152—153°, and decomposes at 190°; the corresponding bromo- and chloro-derivatives melt at 152—153° and 153—154° respectively. It is decomposed by concentrated sulphuric acid, but dissolves without change in alkalis and concentrated hydrochloric acid; the rotatory power  $[\alpha]_D = -10.4^\circ$  in 2.5 per cent. alcoholic solution. The *silver salt*,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{ISAg}$ , is amorphous; the *barium salt* crystallises with  $2\text{H}_2\text{O}$ ; the *ethyl salt* forms colourless needles melting at 104—105°. All the salts are dextrogyrate, the rotatory power increasing with the concentration, for the sodium salt,  $[\alpha]_D = +8^\circ$ ;  $+12.7^\circ$ ;  $+16.7^\circ$  for solutions containing 5.327 grams, 10.654 grams and 21.306 grams per 100 c.c. respectively; the corresponding values for the bromo-acid are  $+7^\circ$ ,  $+7^\circ$ ,  $+9.5^\circ$  for solutions containing 5.362 grams; 10.724 grams; and 21.448 grams, equivalent to 5, 10, and 20 grams of free acid respectively. When heated with moderately concentrated sulphuric acid, pariodophenylmercapturic acid is resolved into acetic acid and

iodophenylcysteine,  $\text{NH}_2\cdot\text{CMe}(\text{SC}_6\text{H}_4\text{I})\cdot\text{COOH}$ , the *hydrochloride* of which is deposited in feathery transparent crystals; these readily dissociate in contact with water. By the action of potassium cyanate on iodophenylcysteine, the *uramido-acid*,



is formed, and crystallises in small needles melting at  $195\text{--}196^\circ$ . With acetic anhydride, iodophenylcysteine regenerates the mercapturic acid. When heated with potash, iodophenylmercapturic acid is resolved into ammonia, acetic acid, pyruvic acid and *pariodophenylmercaptan*. The latter crystallises in needles, melts at  $85\text{--}86^\circ$ , has a characteristic odour of aniseed, gives yellow precipitates with copper, lead, and silver salts, and is rapidly oxidised by the air to pariodophenyl bisulphide,  $\text{C}_{12}\text{H}_9\text{I}_2\text{S}_2$ ; this crystallises in plates, melts at  $124^\circ$ , and gives a dark-blue solution when warmed with sulphuric acid. Both compounds were identical with synthetical preparations obtained from iodobenzenesulphonic acid, proof being thus afforded that the iodine is in the *para*-position. Pariodophenylmercapturic acid is thus shown to have the formula



J. B. T.

**Synthesis of the Diphenyl Hydrocarbons: Para- and Ortho-phenyltoluenes.** By GIUSEPPE ODDO and A. CURATOLO (*Gazzetta*, 1895, 25, i, 126—136).—A diazotised mixture of aniline and paratoluidine is slowly added to alcoholic sodium ethoxide, gas is evolved, and, after heating on the water bath in a reflux apparatus, the solution is distilled in a current of steam. The distillate is extracted with ether and the extract evaporated; on fractionally distilling the residue, paraphenyltoluene,  $\text{C}_6\text{H}_4\text{PhMe}$ , is obtained as a colourless liquid, which boils at  $262\text{--}268^\circ$ , and solidifies in a mixture of ice and salt; it is accompanied by small quantities of benzene, toluene, and diphenyl.

By substituting orthotoluidine for its *para*-isomeride in the above process, orthophenyltoluene may be prepared; it is an oil which does not solidify in a mixture of ice and salt, boils at  $261\text{--}264^\circ$ , and yields orthodiphenylcarboxylic acid on oxidation with chromic acid. It readily takes up bromine, yielding a *tribromo*-derivative,  $\text{C}_{13}\text{H}_9\text{Br}_3$ , which crystallises in long, white needles melting at  $167\text{--}169^\circ$ , and is easily oxidised by chromic mixture; by the aid of this compound, it is shown that a very small proportion of orthophenyltoluene is formed by the action of sodium on a mixture of bromobenzene and orthobromotoluene in ethereal solution.

W. J. P.

**Action of Hydrazine Hydrate on Benzoïn and on Deoxybenzoïn.** By THEODOR CURTIUS and A. BLUMER (*J. pr. Chem.*, 1895, [2], 52, 117—137).—*Benzoïnhydrazine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}_2$ , is prepared by warming a mixture of benzoïn (40 grams) and hydrazine hydrate ( $11\frac{1}{2}$  grams) on the water bath for four hours, and then setting it aside for eight days. It crystallises in thick, colourless prisms, melts at  $75^\circ$ , and dissolves in alcohol, ether, chloroform, and benzene, but not in water or alkalis. It reduces Fehling's solution and ammo-

niacal silver nitrate; acid converts it into benzoïn and a hydrazine salt; boiling water also decomposes it.

When benzoïnhydrazine is kept at  $110^{\circ}$  for some hours, and the mass is then extracted with hot alcohol, white needles separate from the alcoholic solution; these have the empirical formula  $C_{14}H_{10}N$ , melt at  $246^{\circ}$ , and sublime unchanged; they dissolve in sulphuric acid with a crimson colour and are reprecipitated on dilution; ether and chloroform dissolve them freely, alcohol sparingly, water and alkalis not at all. From the mother liquor of these crystals, bisbenzoylphenylazimethylene (see below) separates, and is followed by a new compound, probably  $\langle \text{CHPh}\cdot\text{NH}\cdot\text{CHPh} \rangle$ , which melts at  $261^{\circ}$ , sublimes unchanged, and dissolves in strong acids without apparent change; ether dissolves it sparingly, alcohol and chloroform easily. The same compounds are formed when an alcoholic solution of benzoïnhydrazine is heated for many days, or when hydrogen chloride is passed into ether which contains benzoïnhydrazine in suspension.

*Acetylbenzoïnhydrazine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{NHAc}$ , crystallises in white needles and melts at  $132^{\circ}$ . A *monosodium* and a *disodium* derivative of benzoïnhydrazine are described.

*Benzylidenebenzoïnazine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh}$ , obtained by adding benzaldehyde to an alcoholic solution of benzoïnhydrazine, crystallises in white nacreous needles, melts at  $133^{\circ}$ , and dissolves in ether and alcohol, but not in water. *Orthonitrobenzylidenebenzoïnazine* forms white needles, melts at  $195^{\circ}$ , and dissolves in hot alcohol and in ether. *Metanitrobenzylidenebenzoïnazine* crystallises in yellow needles, melts at  $192^{\circ}$ , and dissolves in alcohol and chloroform, sparingly in ether, and not at all in water. *Cuminyllbenzoïnazine* crystallises in yellowish, nacreous laminæ, melts at  $117^{\circ}$ , and dissolves freely in alcohol, ether, and chloroform, but not in water.

*Benzoïnketazine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}\cdot\text{CHPh}\cdot\text{OH}$ , was obtained by the action of benzoïn on benzoïnhydrazine; it is colourless, and melts at  $157^{\circ}$ .

*Bisbenzoylphenylazimethylene*,  $\text{COPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}\cdot\text{COPh}$ , prepared as described above, crystallises in yellow needles, melts at  $202^{\circ}$ , and dissolves in glacial acetic acid, ether, chloroform, and hot alcohol, but not in hydrochloric acid, caustic soda, or water; it distils unchanged. It is precipitated from its solution in strong sulphuric acid unchanged, unless the solution has been kept, in which case benzile and hydrazine sulphate are produced. Reduction with zinc dust in glacial acetic acid converts bisbenzoylphenylazimethylene into benzyl phenyl ketone and ammonia.

*Benzylphenylmethylenehydrazine*,  $\text{CH}_2\text{Ph}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}_2$ , is prepared by heating benzyl phenyl ketone (5 grams) with hydrazine hydrate (1.3 grams) and a couple of drops of alcohol in a sealed tube at  $140^{\circ}$  for five hours; it crystallises in white needles, melts at  $62^{\circ}$ , and dissolves freely in alcohol, ether, and chloroform; it distils unchanged, and reduces ammoniacal silver nitrate and Fehling's solution. This hydrazine is a true secondary hydrazine, undergoing condensation with aldehydes in the cold and with ketones when

warmed. When treated with iodine in alcohol, it is converted into *bisbenzylphenylazimethylene* (*benzylphenylketazine*)



which crystallises in small, straw-coloured needles, melts at  $164^\circ$ , distils unchanged, and dissolves in ether and chloroform, but not in water.

A. G. B.

**The Induline Group.** By OTTO FISCHER and EDUARD HEPP (*Annalen*, 1895, **286**, 187—247; compare Abstr., 1893, i, 333, and this vol., i, 527).—The system of nomenclature already developed (*loc. cit.*) is retained, benzeneindulines, in which the substituent radicle takes up the position R (general formula I) being referred to as *meso*-derivatives.

The most productive source of *meso*-phenylinduline,  $\text{C}_{18}\text{H}_{13}\text{N}_3$ , is *aposafranine* (Abstr., 1893, i, 613). This base is characterised by its green solution in oil of vitriol, the colour of the solution in acid containing the monhydrate or anhydride being brownish-red; the salts form magenta-red solutions in water. The base dissolves readily in methylal, and, on evaporation of the solvent, is deposited as a crystalline crust, having a beautiful, dark green reflex; when dry, it may be heated at  $100^\circ$  without undergoing change, but, on boiling the solution in benzene, a powder separates, forming a brown solution in concentrated sulphuric acid, and dissolving with difficulty in the dilute acid or in acetic acid, yielding reddish-violet solutions. At the same time, a small quantity of *meso*-phenylinduline is formed, this being most readily obtained by heating *aposafranine* hydrochloride with aniline in the manner already described (*loc. cit.*). The *nitrate* of *meso*-phenylinduline crystallises from alcohol in lustrous, green needles; the *platinochloride* forms slender crystals having a dark green reflex, and the *aurochloride* crystallises in lustrous, green needles. The base itself, which has also been called *amidoazobenzeneinduline*, melts at  $203\text{--}204^\circ$ , and not at  $215^\circ$  as previously stated (*ibid.*, 335); the action of a mixture of glacial acetic and hydrochloric acids, during six hours at  $160\text{--}170^\circ$ , gives rise to benzeneindone hydrate, whilst treatment with alcoholic barium hydroxide for 10 hours at  $140\text{--}145^\circ$  converts it into benzeneindone (Abstr., 1892, 341). *Phenylmesophenylinduline*,  $\text{C}_{24}\text{H}_{17}\text{N}_3$ , has already been described as the product of the action of aniline on *mesophenylinduline*, and is most conveniently obtained by heating *aposafranine* with aniline for an hour at  $150\text{--}160^\circ$ ; *paratolylmesoparatolylinduline* has been prepared by a similar process, and melts at  $227\text{--}228^\circ$ .

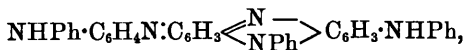
*Phenylmesoamidophenylinduline* (*loc. cit.*) is formed when azophenine (4.5 grams) and paraphenylenediamine hydrochloride (2 grams) are heated with aniline (10 grams) and alcohol (50 grams) for 12 hours at  $140^\circ$ ; this process depends on the oxidation of a mixture of paraphenylenediamine and aniline, and the same principle is probably involved in an alternative method, when these bases are heated at  $150^\circ$  with quinonedianil. The base is primary in character, and the *formyl* derivative crystallises in bluish-green leaflets, which transmit red light, and melt at  $230^\circ$ ; the *monacetyl* derivative softens

at 150° and melts at 160°, and yields an *acetate* which melts and decomposes at 183°.

Unsymmetrical *hydroxybenzeneindone* is obtained by heating phenyl-mesoamidophenylinduline with alcoholic barium hydroxide for 3½ hours at 180—200°, and is freed from mesohydroxyphenylinduline by treatment with dilute hydrochloric acid, which precipitates the latter base; the crystalline substance has a bronze lustre, and the solution in concentrated sulphuric acid is brownish-red, becoming orange on dilution. The dilute solution in alkalis is red, and exhibits greenish fluorescence, which is also noticeable in the alcoholic solution. The *hydrochloride* of mesohydroxyphenylinduline, which is formed at the same time, separates from glacial acetic acid on the addition of water in lustrous, green crystals; the solution in concentrated sulphuric acid is green, becoming brownish-red and finally red on dilution, whilst the red, alcoholic solution exhibits feeble, brown fluorescence.

The *benzylidene* derivative of phenylmesoamidophenylinduline crystallises from the dark red, alcoholic solution in small needles, having a green reflex; it melts at 261—262°, and in the finely divided state has electrical properties and transmits red light. The *ortho*hydroxybenzylidene compound crystallises in dark brown leaflets transmitting reddish-yellow light.

As already suggested, the mauveïnes and indazines are to be regarded as symmetrical indulines, having the general formula  $\text{NH}\cdot\text{C}_6\text{H}_3\langle\text{N}^-\text{NR}\rangle\text{C}_6\text{H}_3\cdot\text{NH}_2$ . In preparing dimethylmauveïne from nitrosodimethylaniline and diphenylmetaphenylenediamine, a *base*,  $\text{C}_{28}\text{H}_{27}\text{N}_5$ , is obtained; this dissolves in benzene, forming a violet solution, and, on evaporating the solvent, is deposited as a lustrous, green, crystalline powder, which contains benzene and melts at 178°; when this is heated in the vapour of boiling xylene, the benzene is removed, and the substance then melts at 210—212°. The formation of two bases is also observed when nitrosomonomethylaniline, nitrosomonethylaniline, or nitrosodiethylaniline is heated with diphenylmetaphenylenediamine. Thus, *phenylamidophenylmauveïne*,

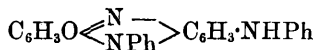


is formed, together with phenylmauveïne, when nitrosodiphenylamine (28 grams) and diphenylmetaphenylenediamine (26 grams) are heated with 40 per cent. hydrochloric acid (5·5 grams) and alcohol (800 grams) on the water bath, and allowed to remain for 20 hours at the ordinary temperature; the crystals have a bronze lustre, and the substance sinters at 175°, and melts and decomposes at 202°. *Phenylmauveïne*,

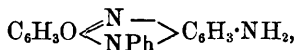
$\text{NH}\cdot\text{C}_6\text{H}_3\langle\text{N}^-\text{NPh}\rangle\text{C}_6\text{H}_3\cdot\text{NHPh}$ , can be obtained from the mother liquor. The solution of this base in concentrated sulphuric acid is grass green, a greenish-blue coloration being developed when phenylamidophenylmauveïne is dissolved in concentrated sulphuric acid; it is less readily soluble in benzene than the foregoing base, the solution being reddish-violet, and depositing the base in crystals which

contain the solvent. After being dried at  $140^{\circ}$ , the base melts at  $256-257^{\circ}$ .

Symmetrical *B*<sub>2</sub>-4-*anilidobenzeneinduline* (mauvindone),



(Abstr., 1893, i, 464), dissolves only sparingly in benzene and toluene, but is more readily soluble in alcohol, and is deposited from a mixture of benzene and alcohol as a crystalline powder with bronze lustre; the solution in concentrated sulphuric acid is bluish-violet, becoming red on dilution. When the base is heated with alkalis, or when phenylmauveine is heated with alcoholic barium hydroxide for 5—10 hours at  $180^{\circ}$ , symmetrical *hydroxybenzeneindone* is formed, and this is found to be identical with safranin obtained by the action of alcoholic potash on phenosafranine, which is converted first into the symmetrical induline, yielding *amidobenzeneindone*,



on protracted treatment with alcoholic potash. From benzene containing some alcohol, it crystallises in magnificent prisms, having a green lustre; the base is somewhat soluble in water, and the solution in concentrated sulphuric acid is violet, becoming pale brown on dilution. When aposafranine is heated with alcoholic potash for 16 hours, a certain amount of benzeneindone hydrate is formed, together with a blue colouring matter.

According to this method of preparation, safranin contains only one hydroxyl group, although Nietzki and Otto have regarded it as a dihydroxy-derivative; moreover, the ethers contain only one ethyl group and are insoluble in alkalis. The *ethyl ether* crystallises from alcohol in prisms having a bronze lustre; it melts and decomposes at  $265^{\circ}$ , and dissolves in concentrated sulphuric acid with a reddish-brown coloration, becoming yellow on dilution. The alcoholic solution is red, and exhibits feeble, brown fluorescence. The *methyl ether* melts at  $240^{\circ}$ .

*Mononitrophenylrosinduline* is obtained by adding potassium nitrate to a solution of phenylrosinduline in concentrated sulphuric acid and heating the liquid at  $50-60^{\circ}$ ; it crystallises in almost black leaflets with a green reflex, sinters at  $250^{\circ}$ , and melts at  $270^{\circ}$ . The solution in concentrated sulphuric acid is green. *Trinitrophenylrosinduline* is formed on adding fuming nitric acid to a solution of phenylrosinduline in glacial acetic acid; it crystallises from nitrobenzene in red leaflets or needles. These nitro-derivatives yield rosindone and nitranylins when heated with glacial acetic acid and concentrated hydrochloric acid for some hours at  $180-200^{\circ}$ . *Mononitrorosindone* separates from its solution in nitrobenzene in dark red crystals, and from glacial acetic acid in bright red needles; the solution in concentrated sulphuric acid is violet. *Amidorosindone* crystallises from ether in lustrous, dark blue leaflets; it forms two series of salts, one being blue, the other reddish-yellow.

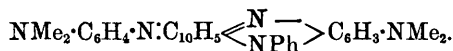


Nt<sub>2</sub>-3'-Hydroxyrosindone, C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>, is formed when sodium phenylrosindulinesulphonate is heated with 10 per cent. sodium hydroxide (10 parts) at 220°, the sodium salt separating in red leaflets as the liquid cools. The compound crystallises from alcohol in prisms having a dark, brownish-green reflex; the alcoholic solution exhibits greenish fluorescence, and the solution in concentrated sulphuric acid is reddish-violet, becoming yellow on dilution.

Nt<sub>2</sub>-2'-Hydroxyrosindone is obtained by the same method from the corresponding sulphonic acid, forming a sodium salt which crystallises in lustrous leaflets, and dissolves in 400 parts of water. The hydrochloride crystallises in compact, red prisms having a green reflex, and the alcoholic solution exhibits greenish-yellow fluorescence. Hydroxyrosindone crystallises from alcohol in yellowish-red leaflets; its solution in concentrated sulphuric acid is magenta coloured, in alkalis brownish-yellow, and in alcohol greenish-yellow, exhibiting fluorescence of the same tint.

Symmetrical anilidophenylinduline is prepared by gently heating a mixture of nitrosophenyl- $\alpha$ -naphthylamine hydrochloride, and diphenylmetaphenylenediamine dissolved in alcohol; the green liquid soon becomes blue, and is then set aside for 12 hours. The base separates as a bluish-violet powder, and crystallises from benzene in leaflets having a greenish lustre. The hydrochloride is deposited from the alcoholic solution as a bluish-violet, crystalline powder. When the salt is heated with glacial acetic acid and concentrated sulphuric acid for nine hours at 200–220°, B<sub>2</sub>-4-hydroxyrosindone is formed, this substance being also produced by the action of hydrochloric and glacial acetic acids on amidophenylrosinduline (*ibid.*, 335).

The compound obtained from nitrosodimethylaniline,  $\alpha$ -naphthylamine hydrochloride, and aniline, which was regarded as B<sub>1</sub>-dimethylisorosinduline (*ibid.*, 336), has, in reality, the constitution



This view of its structure receives support from the conversion of the substance into B<sub>2</sub>-4-hydroxyrosindone by means of hydrochloric acid at 180°, and also from its formation by the action of nitrosodimethylaniline on  $\beta$ -phenylnaphthylamine, as, from the constitutional formula now put forward, it is seen to be a derivative of  $\beta$ -phenylnaphthylamine. The action of nitrosodimethylaniline on  $\beta$ -phenylnaphthylamine gives rise to an isomeride which forms reddish-brown crystals, the solution in alcohol being reddish-violet, and becoming magenta-red when treated with mineral acids; the solution in concentrated sulphuric acid is green, but neither the base nor its salts exhibits fluorescence in solution.

When benzeneazo- $\alpha$ -naphthylamine hydrochloride is heated with phenol for an hour at 120–130°, rosinduline, C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>, and "naphthyl red," C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>, are produced (*ibid.*, i, 721). The former is separated by means of the ready solubility of its hydrochloride in dilute alcohol; it crystallises from benzene in aggregates of leaflets and melts at 198–199°. Naphthyl-red is a brownish-red, crystalline

substance, having a green iridescence; it is somewhat soluble in hot water, and absorbs carbonic anhydride from the air. The *hydrochloride* crystallises from dilute alcohol in long, golden needles; the solution in concentrated sulphuric acid is yellowish-green, becoming pink and finally reddish-violet on dilution. Although not very soluble in cold water, the reddish-violet solution exhibits an intense fluorescence resembling that of Magdala red. The *platinochloride* is a brown, crystalline powder.

Nt<sub>2</sub>-4-Amidonaphthindone, C<sub>26</sub>H<sub>17</sub>N<sub>3</sub>O, is obtained by heating the hydrochloride of naphthyl-red with glacial acetic acid and concentrated hydrochloric acid for nine hours at 190–200°; it crystallises from alcohol in beautiful, green plates. The solutions in alcohol and benzene exhibit fiery-red fluorescence, and the solution in concentrated sulphuric acid is blue by reflected, red by transmitted light, becoming brownish-yellow, and, finally, red on dilution. The *hydrochloride* crystallises in needles with a bronze lustre. The Nt<sub>2</sub>-4-hydroxynaphthindone, obtained by decomposing anilidophenylnaphthinduline, is also formed when the hydrochloride of naphthyl-red or amidonaphthindone is heated with acetic and hydrochloric acids for about 20 hours at 200–220°.

When commercial Magdala red is covered with hot benzene, heated with alcoholic potash for 15 minutes, filtered, and again boiled with benzene, it is separated into two bases, one of which, C<sub>30</sub>H<sub>19</sub>N<sub>3</sub>, remains dissolved in the benzene, whilst the residue consists of the amido-derivative, C<sub>30</sub>H<sub>20</sub>N<sub>4</sub>. The solution of the former in concentrated sulphuric acid is blue, but the addition of a few drops of water causes the liquid to appear yellowish-green by transmitted light and pink by reflected light. The second base forms a yellowish-green solution in concentrated sulphuric acid, the liquid becoming brownish-pink and ultimately red on dilution, whilst both bases exhibit fluorescence in alcoholic solution. The base C<sub>30</sub>H<sub>19</sub>N<sub>3</sub>, symmetrical *meso-α-naphthyl-naphthinduline*, crystallises from benzene in brownish-red leaflets; when heated with glacial acetic and concentrated hydrochloric acids for 15 hours at 220°, it yields *meso-naphthyl-naphthindone*, C<sub>10</sub>H<sub>5</sub>O  $\left\langle \begin{smallmatrix} \text{N} \\ \text{N}(\text{C}_{10}\text{H}_7) \end{smallmatrix} \right\rangle$  C<sub>10</sub>H<sub>5</sub>, which separates from alcohol in prismatic crystals, and dissolves in concentrated sulphuric acid with a bluish-green coloration.

Magdala red is obtained from the residue left by the commercial substance after treatment with alcoholic potash and benzene; when this is dissolved in alcohol with the addition of sulphuric acid, the sulphate is obtained in crystals with a bronze reflex. The base, C<sub>30</sub>H<sub>20</sub>N<sub>4</sub>, crystallises in small prisms with a green reflex; they contain ether, but this is completely removed in the vapour of boiling xylene; it dissolves sparingly in benzene and ether, but is more readily soluble in methylal. The aqueous and alcoholic solutions do not exhibit fluorescence, but they absorb carbonic anhydride from the air, developing a vivid red fluorescence which disappears on the addition of alkalis. When the alcoholic solution of the sulphate is treated with sulphuric acid and sodium nitrite, the base, C<sub>30</sub>H<sub>19</sub>N<sub>3</sub>, is formed. When heated with glacial acetic and concentrated hydro-

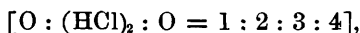
chloric acids for 20 hours at 200—210°, *amido-meso-naphthyl-naphthindone* is formed, and crystallises in needles; the solution of this in concentrated sulphuric acid is blue by reflected, red by transmitted light, and, when diluted, becomes violet, and ultimately red. *Hydroxy-meso-naphthyl-naphthindone*,  $C_{30}H_{18}N_2O_2$ , formed at the same time, separates from alcohol in prismatic crystals having a green lustre; its solution in concentrated sulphuric acid is blue, becoming first carmine, and then yellowish-red on dilution. The *hydrochloride* forms red crystals with a green reflex; the alcoholic solution is yellowish-red, and when dilute exhibits a green fluorescence.

The paper concludes with a table in which the various indones investigated by the authors are collected, together with their principal colour reactions. M. O. F.

**Naphthazarin.** By THEODOR ZINCKE and M. SCHMIDT (*Annalen*, 1895, **286**, 27—57; compare this vol., i, 150).—The *diacetyl* derivative of naphthazarin crystallises from hot, glacial acetic acid in lustrous, golden-yellow needles, and melts at 189°; it dissolves in concentrated sulphuric acid with development of a red coloration, and is slowly hydrolysed by alkalis.

1 : 4 : 1' : 2'-*Tetrahydroxynaphthalene* is obtained by reducing naphthazarin, suspended in alcohol, with stannous chloride and hydrochloric acid; it crystallises from alcohol in yellow needles, and melts and becomes red at 154°. Very dilute solutions in common solvents exhibit a greenish fluorescence, and the aqueous solution becomes red on exposure to air; the solution in concentrated sulphuric acid is greenish-yellow. The tetracetyl derivative has been already obtained (*loc. cit.*). Tetrahydroxynaphthalene rapidly undergoes oxidation when an alkaline solution is exposed to air, treatment with aqueous sodium hydroxide giving rise to a green salt, which gradually yields a blue solution, from which the sodium derivative of naphthazarin separates in coppery leaflets. Attempts to convert tetrahydroxynaphthalene into a diquinone were unsuccessful, the substance being indifferent towards nitrous acid, atmospheric oxygen, and nitric acid, whilst ferric chloride oxidises it to naphthazarin.

The *dichlorinated* additive compound of naphthazarin



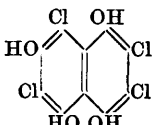
is prepared by the action of dry chlorine on naphthazarin suspended in cold chloroform; it crystallises in dark-yellow, compact prisms, and decomposes at 220°. When treated with boiling alcohol, 1 mol. HCl is eliminated, and alkalis and alkali carbonates convert it into the blue sodium derivative of monochloronaphthazarin.

*Monochloronaphthazarin* is obtained by dissolving the dichlorinated additive compound in boiling glacial acetic acid, and heating on the water bath with sodium acetate dissolved in the minimum quantity of water; it crystallises from hot glacial acetic acid in greenish-black needles having a metallic lustre, and melts at 176°. The *diacetyl* derivative crystallises from acetic anhydride in golden-yellow needles, and melts at 192°; it is formed when chlorine acts on the *diacetyl* derivative of naphthazarin.

*Hexachlorotetraketohexahydronaphthalene*, , is prepared

by suspending monochloronaphthazarin in glacial acetic acid, saturating the liquid with chlorine, and vigorously agitating it in a closed vessel; it crystallises from benzene in small, pale yellow needles, and from glacial acetic acid in prismatic crystals. It dissolves in hot, fuming nitric acid, from which it separates in yellow crystals; the solution in concentrated sulphuric acid is red.

*Tetrachloronaphthazarin* is obtained from the foregoing compound by reducing it in hot glacial acetic acid solution with stannous chloride; it is also formed when the hexachloro-derivative is heated with hydrochloric acid at 160° for 10–12 hours, dichloromaleic acid being produced at the same time. It crystallises from glacial acetic acid in dark red, lustrous plates, and melts at 244°; the salts are deep blue, and dissolve with difficulty in water and alcohol. The compound is indifferent towards alkalis, this behaviour being probably due to the sparing solubility of the alkali salts; these, however, yield naphthazarin very easily when a solution in alcohol or glacial acetic acid is heated with zinc dust. The *acetyl* derivative crystallises from acetic anhydride in golden-yellow needles, and melts at 244°. *Anilido-trichloronaphthazarin* is formed when a solution of the tetrachloro-derivative in glacial acetic acid is boiled with aniline; it crystallises from the acid in brown needles, and melts at 224°. The alkali salts are blue, and the solution in concentrated sulphuric acid is blue, becoming red when heated. The action of chlorine on tetrachloronaphthazarin, dissolved in glacial acetic acid, converts it into the hexachloro-derivative already described; the same effect is produced by bleaching powder.

*Tetrachlorotetrahydroxynaphthalene*, , is obtained by

the action of stannous chloride on the hexachloro-derivative and tetrachloronaphthazarin; the product is separated as rapidly as possible, and excess of the reducing agent must be avoided.

Solutions of the compound in alkalis are green, the surface of the liquid rapidly becoming coated with a blue, coppery oxidation product. The *tetracetyl* derivative crystallises from acetic anhydride in slender, colourless needles, and melts at 250°.

*Tetrachlorotetraketotetrahydronaphthalene* is formed when the hexachloro-derivative is cautiously melted, chlorine being evolved. It sublimes when strongly heated, and crystallises in lustrous, yellow leaflets resembling mosaic gold in appearance; common solvents and fuming nitric acid dissolve it with difficulty. Reduction in glacial acetic acid with stannous chloride gives rise to tetrachloronaphthazarin, tetrachlorotetrahydroxynaphthalene being formed when excess of the reducing agent is employed; tetrachloronaphthazarin is also

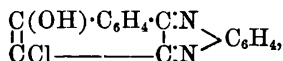
formed by the action of hot hydrochloric acid. The quinone dissolves in hot quinoline or phenol, giving rise to red compounds. Orthophenylenediamine unites with it, forming an *eurhodole* which is isomeric with the similar compound obtained from tetrachloronaphthazarin, the alcoholic solution being blue, and the ammonium salt sparingly soluble. Aniline converts the quinone into the *dianilido*-derivative, which crystallises from glacial acetic acid in needles having a metallic lustre; the solution in aqueous soda is violet. Concentrated hydrochloric acid at 150° removes one aniline group, which appears to be replaced by an atom of chlorine.

The *eurhodole* obtained from tetrachloronaphthazarin by the action of orthophenylenediamine crystallises in greenish-brown leaflets and needles exhibiting a metallic lustre; it does not melt below 250°, and dissolves with difficulty in common solvents. The *sodium* salt is violet, and dissolves sparingly in alkalis, the solution in alcohol being blue. The *triacyl* derivative crystallises in yellowish, microscopic prisms, and does not melt below 250°. Another *acyl* derivative is obtained by boiling the alcoholic solution of diacetyltetrachloronaphthazarin with orthophenylenediamine; it yields the triacyl derivative when treated with boiling acetic anhydride.

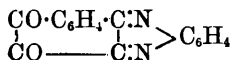
In order to compare the properties of tetrachloronaphthazarin with the behaviour of  $\alpha$ -naphthaquinone derivatives towards orthophenylenediamine, the following compounds have been prepared.

$\alpha\beta$ -Dichloronaphthaphenazine,  $\begin{array}{c} \text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{C}:\text{N} \\ | \\ \text{Cl} \text{---} \text{C}:\text{N} \end{array} > \text{C}_6\text{H}_4$ , is obtained by adding orthophenylenediamine to a hot solution of dichloro- $\beta$ -naphthaquinone in glacial acetic acid; it crystallises in slender, yellow needles, and melts at 202°.

$\alpha\beta$ -Hydroxychloronaphthaphenazine ( $\beta$ -chloronaphtheurhodole),



is prepared by the action of the base on dichloro- $\alpha$ -naphthaquinone and hydroxychloro- $\alpha$ -naphthaquinone; it crystallises in brownish-red needles which exhibit a metallic lustre. The solution in hot, aqueous soda is red; dilute aqueous alkali dissolves it when cold, further addition of soda causing separation of the sodium derivative in yellowish-red leaflets and needles having a greenish lustre. Nitric acid (sp. gr. 1.4) oxidises the *eurhodole* to *diketonnaphthaphenazine*,

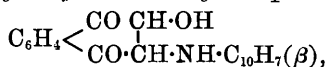


(following abstract).

M. O. F.

**$\alpha\alpha$ -Diketotetrahydronaphthalene Oxide.** By THEODOR ZINCKE and P. WIEGAND (*Annalen*, 1895, 286, 58–89; compare Abstr., 1893, i, 220).—Diketotetrahydronaphthalene oxide combines readily with bases, the compounds obtained by the action of aniline having already been described (*loc. cit.*).

*β-Naphthylamidohydroxydiketotetrahydronaphthalene*,

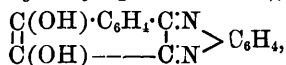


crystallises in needles with a golden lustre; when heated alone, or when treated with boiling glacial acetic acid, it is converted into *β-naphthylamidohydroxy-α-naphthaquinone*, which crystallises in dark blue leaflets, and melts at 178°.

*Paratoluidohydroxy-α-naphthaquinone* crystallises in deep blue, lustrous leaflets, and melts at 188°; the odour of isocyanide becomes perceptible on dissolving it in aqueous alkali. The *ortho*-derivative melts at 172°.

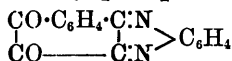
*α-Naphthylamidohydroxy-α-naphthaquinone* crystallises from glacial acetic acid in bluish-black leaflets, and melts at 174°; bromine converts it into the *tetrabromo*-derivative melting at 114°; a small quantity of *isonaphthazarin* is formed at the same time.

When an alcoholic solution of *diketotetrahydronaphthalene oxide* is heated on the water bath with *orthophenylenediamine*, a mixture of three products is obtained. The compound  $\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \equiv \text{N} - \\ | \\ \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{NH} \end{array} > \text{C}_6\text{H}_4$  separates from the liquid in brownish-red needles after a few hours; at 150° it becomes blue and decomposes, yielding *αβ-dihydroxy-naphthaphenazine* (*αβ-hydroxynaphthetheurhodole*),



a deep blue, crystalline powder which melts at 241°. This substance is formed when an alcoholic solution of *diketotetrahydronaphthalene oxide* is heated with *orthophenylenediamine* for half an hour, and can also be prepared from the foregoing compound by treatment with boiling glacial acetic acid, and by the action of aqueous soda or concentrated sulphuric acid; the sodium derivative is green and the sulphate red. The *diacetyl* derivative crystallises in white, lustrous needles, and melts at 208°, a red *monacetyl* derivative being produced when the action of boiling glacial acetic acid is interrupted before the formation of the *diacetyl* compound. *αβ-Dihydroxynaphthaphenazine* is converted into *αβ-naphthaphenazine* by cautiously heating it with zinc dust in an atmosphere of hydrogen.

*αβ-Diketonaphthaphenazine* (*naphthaphenazinequinone*),



is prepared by oxidising *dihydroxynaphthaphenazine* in glacial acetic acid solution with nitric acid of sp. gr. 1.4; it crystallises in golden-yellow needles, and melts and decomposes at 265°. On reducing it with stannous chloride, the *dihydroxy*-derivative is regenerated. The *monoxime* crystallises in yellowish-green needles, and melts and decomposes at 219°.

*Naphthadiphenazine*,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ | \\ \text{N} \cdot \text{C} - - - \text{C} \cdot \text{N} \end{array} > \text{C}_6\text{H}_4$ , is the third pro-

duct of the action of orthophenylenediamine on diketotetrahydro-naphthalene oxide; it crystallises from glacial acetic acid in slender, white needles, and does not melt below  $275^{\circ}$ . Mineral acids yield yellow or red salts which are decomposed by water and on exposure to air.

*Benzeneazo- $\beta$ -naphthaquinol* (1 : 3 : 4-benzeneazodihydroxynaphthalene),  $\begin{array}{c} \text{C(OH)} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \\ | \\ \text{C(OH)} - \text{CH} \end{array}$  or  $\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \\ | \\ \text{C(OH)} = \text{CH} \end{array}$ , is obtained by

treating a solution of diketotetrahydro-naphthalene oxide in hot, glacial acetic acid with phenylhydrazine in the same solvent; it is also formed on adding the theoretical quantity of diazobenzene chloride to a solution of  $\beta$ -naphthaquinol in alcohol. The substance is dark red; it melts and froths at  $214^{\circ}$ . The solution in alkalis is blue, rapidly becoming brownish-red, whilst concentrated sulphuric acid dissolves it, developing a deep blue coloration. The *hydrochloride* separates from the blue solution in lustrous, green needles, which closely resemble magenta; it is rapidly decomposed by alcohol, and less easily by water, undergoing but slight change on exposure to air. The *monacetyl* derivative crystallises from hot benzene in red, lustrous needles, and melts at  $133^{\circ}$ ; it is insoluble in cold aqueous alkali, undergoing hydrolysis when heated, this result being also produced by hydrochloric acid. The *diacetyl* derivative is formed when sodium acetate is employed; it crystallises from hot alcohol in orange plates, and melts at  $153^{\circ}$ . It is easily reduced in alcoholic solution by treating it with zinc dust and glacial acetic acid, the *diacetyl* derivative of benzenehydrazo- $\beta$ -naphthaquinol being formed; this crystallises in colourless needles, and melts at  $178^{\circ}$ . It is insoluble in aqueous alkalis, but is converted into benzeneazo- $\beta$ -naphthaquinol by alcoholic potash. When benzeneazo- $\beta$ -naphthaquinol is reduced, in alcoholic solution, with zinc dust and glacial acetic acid, it is resolved into aniline and amidodihydroxynaphthalene, the latter being immediately oxidised to hydroxyimidonaphthol,  $\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{NH} \\ | \\ \text{C(OH)} : \text{CH} \end{array}$ .

*Benzeneazo- $\beta$ -naphthaquinone* (1 : 3 : 4-benzeneazodiketodihydro-naphthalene),  $\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \\ || \\ \text{CO} - \text{CH} \end{array}$ , is obtained by allowing an alkaline solution of benzeneazo- $\beta$ -naphthaquinol in alcohol to remain in an atmosphere of oxygen; the deep blue liquid becomes brown, and the product separates in long, yellow needles. When recrystallised from ether, it melts and evolves gas at  $250^{\circ}$ . The quinol is regenerated when the alcoholic solution is heated with alkali.

The phenylhydrazone of hydroxynaphthaquinone has been already investigated by Zincke and Thelen, and more recently by Kostanecki; the monacetyl and diacetyl derivatives melt at  $173^{\circ}$  and  $123^{\circ}$  respectively. On reducing the diacetyl derivative in alcoholic solution with zinc dust and glacial acetic acid, 1 : 2 : 4-*amidodihydroxynaphthalene* is produced, forming aggregates of colourless crystals; it becomes violet at  $130^{\circ}$ , and melts to a blue liquid at  $162^{\circ}$ . It becomes blue on exposure to air, and the solutions in common solvents rapidly

acquire the same colour. The *hydrochloride* crystallises in nacreous leaflets, and forms a green solution in alkalis, ammonia being evolved; on exposure to air, the solution becomes brownish-red, and yields hydroxynaphthaquinone when treated with acids. Acetanilide is a product of the reduction of the diacetyl derivative, whilst aniline is formed, together with amidodihydroxynaphthalene, when the mon-acetyl derivative is reduced. M. O. F.

**Azo Colouring Matters.** By EUGEN BAMBERGER and FRANZ MEIMBERG (*Ber.*, 1895, 28, 1887—1897).—Bamberger's statement (this vol., i, 351) that normal and iso-diazo-compounds yield identical products, is now shown to be true for the products obtained by the action of methylaniline and of ethylaniline on normal and iso-paranitrodiazobenzene.

The authors confirm Hantzsch's statement (this vol., i, 418) that the two isomeric paranitrophenylazo- $\alpha$ -naphthols, obtained by treating paranitrodiazobenzene hydrate with  $\alpha$ -naphthol, are position isomerides, being respectively para- and ortho-derivatives of naphthalene.

The following new compounds are described.

*Orthonitrophenylparazo- $\alpha$ -naphthol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystal-  
(1) (4, 2) (1)  
lises in dark red needles, which have a bronzy lustre. It decomposes and melts at 244—245°, and is readily soluble in hot xylene and amyl alcohol. When reduced, and then treated with ferric chloride, it gives  $\alpha$ -naphthaquinone.

*Orthonitrophenylortho- $\alpha$ -naphthol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is  
(1) (2, 2) (1)  
formed, together with the above para-compound, when orthonitrodiazobenzene methyl ether is treated with  $\alpha$ -naphthol. It crystallises in brownish-red, glistening needles, melts at 215—216°, and is soluble in concentrated sulphuric acid. It does not yield  $\alpha$ -naphthaquinone. Both the ortho-compound and the para-compound are soluble in aqueous alkalis.

*Paranitrophenylazodiethylorthotoluidine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NEt}_2$ ,  
(1) (2)  
forms dark orange-red needles, which have a brilliant lustre, and melt at 107.5—108°. Diethylorthotoluidine, however, gives no dye with paranitroisodiazobenzene.

When paranitrophenylazomethylaniline, dissolved in acetic acid, is added to  $\alpha$ -naphthylamine and the mixture is allowed to remain, Meldola's paranitrophenylazo- $\alpha$ -naphthylamine (m. p. 251—252°) separates.  $\alpha$ - and  $\beta$ -naphthol are also capable of replacing the aniline group from both paranitrophenylazo-methylaniline and -ethyl-aniline.

It is also shown that when diazobenzene chloride reacts with alkaline  $\alpha$ -naphthol, 33 per cent. of bisphenylazo- $\alpha$ -naphthol is formed; this fact has been overlooked by previous investigators. The compound melts at 190—191°, whereas Krohn (*Abstr.*, 1889, 152) gives 183° as the melting point.

*Bisparatolylazo- $\alpha$ -naphthol* is formed, together with paratolylazo- $\alpha$ -naphthol, by the action of diazotoluene chloride on an alkaline



solution of  $\alpha$ -naphthol. It is insoluble in alkalis, and crystallises in dark violet needles which melt at  $205-206^\circ$ .

*Bisparabromophenylazo- $\alpha$ -naphthol*,  $\text{OH}\cdot\text{C}_{10}\text{H}_7(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})_2$ , crystallises in green, glistening needles, which melt at  $233-235^\circ$ . It is sparingly soluble in alcohol, ether, and chloroform, but readily in hot benzene or toluene.

According to the authors, *parabromophenylazo- $\alpha$ -naphthol* crystallises in dark brown needles with a greenish iridescence, and melts at  $237-238^\circ$ , and not at  $185^\circ$  or  $195-196^\circ$ , as Margary (Abstr., 1885, 546) states. J. J. S.

**Naphthylindoxazen.** By R. J. KNOLL and PAUL COHN (*Ber.*, 1895, 28, 1872-1873).—The *oxime* of orthobromophenyl naphthyl ketone (this vol., i, 477) is obtained when an alcoholic solution of the ketone is heated for 196 hours with an excess of hydroxylamine hydrochloride and a few drops of hydrochloric acid in a soda-water bottle; the yield is not good, as a considerable portion of the ketone remains unaltered. The oxime, which crystallises in small needles, melts at  $165^\circ$ , and is only sparingly soluble in alcohol or light petroleum, but readily in ethylic acetate. It is not soluble in alkalis, and does not reduce Fehling's solution. When the oxime is heated with alcoholic potash, *naphthylindoxazen*,  $\text{C}_6\text{H}_4\langle\frac{\text{C}(\text{C}_{10}\text{H}_7)}{\text{O}}\rangle\text{N}$ , is formed; this crystallises in small needles, which melt sharply at  $92-93^\circ$ . J. J. S.

**Terpenes and Ethereal Oils.** By OTTO WALLACH (*Annalen*, 1895, 286, 90-118; compare Abstr., 1894, i, 46, also Semmler, *ibid.*, 339).

By OTTO WALLACH and O. SCHARFENBERG.—The authors enumerate reasons for regarding thujone, tanacetone, and salvone as chemically identical, and attribute the difference in their physical properties to admixture with foreign substances. For the purposes of this investigation, thujone has been prepared from oils of thuja, tansy, wormwood, and sage; the ethereal oil of *Artemisia Barrelieni* is also a profitable source of the ketone. Three isomeric thujonoximes have been prepared, and the respective amines obtained on reduction are found to be individual substances.

Thujonoxime, melting at  $90^\circ$ , is obtained by treating the isomeric oxime (m. p.  $54-55^\circ$ ) with phosphorus pentachloride (*loc. cit.*); it crystallises from light petroleum in large, transparent, monoclinic prisms;  $a : b : c = 1.285 : 1 : 1.377$ ,  $\beta = 116^\circ 28'$ . The alcoholic solution is feebly dextrorotatory. Unlike the isomerides, the oxime is not volatile in an atmosphere of steam. When thujonoxime, melting at  $54-55^\circ$ , is dissolved in concentrated sulphuric acid maintained at a temperature below  $50-60^\circ$ , it is converted into an optically inactive *isomeride*, which crystallises from methylic alcohol in long needles and melts at  $119-120^\circ$ ; it dissolves readily in water, and is volatile in an atmosphere of steam, slowly becoming hydrolysed when treated with boiling dilute acids.

*Thujonamine*, obtained by reducing with sodium and alcohol the oxime melting at  $54-55^\circ$ , boils at  $195^\circ$ , has a sp. gr. of 0.8735 and a refractive power  $[n]_D = 1.4608$  at  $20^\circ$ , being identical with tanacetyl-

amine obtained by reducing tanacetoxime (Semmler, Abstr., 1893, i, 107). It absorbs carbonic anhydride with great readiness, forming the *carbonate*, which melts at 106—107°; the *nitrate* and *hydrochloride* melt at 167—168° and 260—261° respectively. The *phenylcarbamide* crystallises in white prisms and melts at 120°.

The *isomeride* obtained from the oxime melting at 90° boils at 193°, and has a sp. gr. of 0.875 and a refractive power  $[n]_D = 1.4625$  at 20°; it absorbs carbonic anhydride slowly. The *nitrate* and *hydrochloride* melt at 124° and 216° respectively, and the *phenylcarbamide* melts at 110°.

The *isomeride* (*isothujonamine*) obtained from the oxime melting at 119—120°, boils at 200—201°, and has a sp. gr. of 0.865 and a refractive power  $[n]_D = 1.468$  at 20°; it absorbs carbonic anhydride very feebly. The *nitrate* and *hydrochloride* melt at 163° and 180—181° respectively; the *carbamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{17}$ , melts at 158—159°, the *phenylcarbamide* crystallises in white needles and melts at 178°, and the *phenylthiocarbamide* crystallises from methylic alcohol in needles and melts at 152—153°.

Thujene (Abstr., 1893, i, 106), obtained by distilling the hydrochloride of thujonamine (from thujonoxime, m. p. 54—55°), is identical with tanacetene prepared by a similar method from tanacetylamine (Semmler, *loc. cit.*). Isothujonamine hydrochloride, when submitted to dry distillation, also yields thujene, which boils at 170—172°, has a sp. gr. of 0.836 and a refractive index  $[n]_D = 1.47145$  at 22°; the identity of this hydrocarbon with thujene obtained from the sources already mentioned has not, however, yet been established. Thujene contains two ethylenic linkings, and differs from all other terpenes in developing an intense, red coloration when a drop of concentrated sulphuric acid is added to its solution in glacial acetic acid.

*Isothujone*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , is obtained by heating thujone with a mixture of concentrated sulphuric acid and water (2 parts) for 8—10 hours in a reflux apparatus, the product being subsequently carried over in a current of steam. The points of difference between thujone, isothujone, and carvotanacetone (Semmler, Abstr., 1894, i, 339) are collected in the following table.

	B. p.	Sp. gr.	$[n]_D$ .	M.
Thujone . . . . .	200—201°	0.9175	1.45109	45.20
Isothujone . . . . .	230—231	0.9285	1.48227	46.69
Carvotanacetone . .	228°	0.9373	1.4835	46.96

Isothujone immediately reduces a cold solution of potassium permanganate; the oxime melts at 119—120°, being identical with the oxime obtained by treating thujonoxime (m. p. 54—55°) with concentrated sulphuric acid; this oxime is invariably obtained from isothujone prepared from oils of thuja, tansy, wormwood, and sage. The ready conversion of thujone into isothujone by means of sulphuric acid suggests a method of separating lævo-fenchone from thujone, as the boiling point of the former is considerably below that of isothujone.

*Dihydroisothujole* or *thujamenthole*,  $\text{C}_{10}\text{H}_{20}\text{O}$ , is obtained by reducing

isothujole with alcohol and sodium; it is a viscous liquid, having the odour of terpineol. It boils at 211—212°, has a sp. gr. of 0.9015 and a refractive power  $[n]_D = 1.46306$  at 20°.

*Thujamenthone*,  $C_{10}H_{18}O$ , is obtained by oxidising the foregoing alcohol in glacial acetic acid solution with chromic anhydride; it boils at 208—211°, has a sp. gr. of 0.897, and a refractive power  $[n]_D = 1.4541$  at 20°. The ketone is isomeric with menthone; it is optically inactive, and has the odour of methone. The oxime melts at 95°, and the *semicarbazide* derivative crystallises in needles and melts at 178°.

Whilst endeavouring to identify thujamenthole and thujamenthone with an alcohol and ketone already known, it was found that tetrahydrocarveol and dihydrocarvotanacetol are identical, but differ from thujamenthole, whilst tetrahydrocarvone is identical with dihydrocarvotanacetone and differs from dihydroisothujole.

When thujone is heated in acetic acid solution with ferric chloride, carvacrol is formed, and the same compound is produced, together with carvotanacetone, when thujone is heated alone at a high temperature.

By OTTO WALLACH and JAMES T. CONROY (Abstr., 1893, i, 598).—When tribromothujone is treated with sodium and methylic alcohol, it yields the compound  $OH \cdot C_{10}H_{11}Br \cdot OMe$ , which forms colourless crystals and melts at 156—157°; it is phenolic in character, forming a nitro-derivative, and the acetyl compound crystallises from methylic alcohol, and melts at 63—64°. The *dimethyl ether*, which melts at 42—43°, is insoluble in alkali, and yields a nitro-derivative by the action of strong nitric acid. The compound,  $OH \cdot C_{10}H_{11}Br \cdot OEt$ , is formed when tribromothujone is dissolved in ethylic alcohol and treated with sodium; it melts at 144—145°, and resembles the methylic compound in general behaviour. An attempt was made to determine the relative position of the oxygen atoms in these compounds. Tribromothujone was dissolved in glacial acetic acid, and heated on the water bath with sodium acetate; on removing the acetic acid, acidifying, and extracting with ether, a product was obtained, which, when oxidised with ferric chloride, yielded a yellow oil having a pronounced odour of quinone. It is, therefore, probable that the hydroxyl groups are in the para-position, and the authors regard the methylic compound (m. p. 156—157°) as having the constitution  $CPr \begin{smallmatrix} \text{CH} - \text{C}(\text{OH}) \\ \text{C}(\text{OMe}) \cdot \text{CBr} \end{smallmatrix} > CMe$ .

M. O. F.

**Terpenes and Ethereal Oils. Brominated Derivatives of the Carvone Series.** By O. WALLACH (*Annalen*, 1895, 286, 119—243).—Racemic *carvone tribromide*,  $C_{10}H_{14}O \cdot HBr \cdot Br_2$ , is obtained by dissolving a mixture of equal quantities of *d*- and *l*-carvone in glacial acetic acid saturated with hydrogen bromide, and having cooled the liquid, adding a solution of bromine in glacial acetic acid; it separates from ethylic acetate in magnificent, monoclinic crystals, and melts at 74—76°. *Lævo*- and *dextro*-carvone tetrabromides melt at 120—122°; the racemic tetrabromide melts at 107—109° (compare Abstr., 1894, i, 538). By the further action of bromine on the liquid from which

the tetrabromides are removed, the  $\alpha$ -pentabromide is formed; the active modifications melt and decompose at 142—143°, and the racemic at 124—126°, the latter being obtained by mixing the lævo- and dextro-pentabromides in equal proportion, and also by the action of bromine on the racemic tetrabromide (m. p. 107—109°). On bromination, dextro-carvone tetrabromide yields the  $\beta$ -pentabromide, which is dextro-rotatory, and melts at 86—87°; the derivative from lævo-carvone tetrabromide has the same melting point, and the racemic  $\beta$ -pentabromide melts at 96—98°. When the carvone bromides are reduced with zinc dust and glacial acetic acid, carvone is regenerated; carvone tetrabromide dissolves in fuming nitric acid, undergoing moderate oxidation when the solution is heated, and yielding a nitrogenous acid, which is decomposed by alkalis with formation of nitrous acid.

On submitting a solution of racemic carvone tribromide in ethylic or amyl alcohol to the action of a current of dry ammonia, an unstable base is formed, of which the salts in aqueous solution yield crystals of a compound having the composition  $C_{10}H_{14}O_2$ ; it separates from alcohol in well-defined crystals, melts at 69—70°, and boils at 123° under a pressure of 10 mm. The substance is insoluble in boiling aqueous soda; it is unsaturated, and the dibromide melts at 94—96°.

*Dihydrocarvone tribromide* is obtained by the action of bromine on the *d*- or *l*-dibromide; it melts at 88—89°, and the racemic modification at 65°.

The ketonic compound,  $C_{10}H_{16}O$ , obtained by heating trihydroxyhydrocymene with dilute sulphuric acid (Abstr., 1894, i, 44), the author calls *carvenone*; on bromination, it yields racemic dihydrocarvone dibromide. The author has already shown (this vol., i, 59) that terpineol may be converted into carvone, and the formation of carvenone from an oxidation product of terpineol affords a means of transforming the alcohol into dihydrocarvone. When dihydrocarvone is heated with dilute sulphuric acid in a reflux apparatus for 10 hours, carvenone is formed, and the production of this substance when trihydroxyhydrocymene is heated with dilute acid depends on the intermediate formation of dihydrocarvone. The abnormal refractive power of carvenone and isothujone has as yet received no explanation, the properties of the substances leaving no doubt as to their ketonic character. Carvacrol is produced when dihydrocarvone and carvenone are oxidised with ferric chloride.

The author discusses the conditions affecting the formation of a racemic compound on mixing *d*- and *l*-modifications; it is found that such combination is almost invariably accompanied by contraction. In connection with this subject, the following crystallographic information has been supplied. Inactive carvone dibromide crystallises in the triclinic system,  $a : b : c = 0.5057 : 1 : 0.5492$ ;  $\alpha = 90^\circ 16'$ ,  $\beta = 107^\circ 18'$ ,  $\gamma = 76^\circ 50'$ . The crystals of *i*-carvone tribromide are monoclinic,  $a : b : c = 0.7154 : 1 : 0.7459$ ;  $\beta = 98^\circ 58'$ . Dextro- and lævo-carvone tribromides form rhombic hemihedral crystals;  $a : b : c = 0.4729 : 1 : 0.7939$ . The *d*- and *l*-carvone tetrabromides also form rhombic hemihedral crystals;  $a : b : c = 0.7078 : 1 : 0.8704$ . The inactive

tetrabromide forms monoclinic crystals;  $a : b : c = 0.7091 : 1 : 0.4605$ ;  $\beta = 100^\circ 32' 45''$ . The *d*- and *l*-carvone tetrabromides form monoclinic hemimorphic crystals;  $a : b : c = 0.7842 : 1 : 0.6006$ ;  $\beta = 98^\circ 6'$ .

M. O. F.

**Essence of Cannabis Indica.** By G. VIGNOLO (*Gazzetta*, 1895, 25, i, 110—114).—The essential oil of *Cannabis indica*, purified by distillation in a current of steam and extraction with ether, is a mobile liquid boiling at  $248$ — $268^\circ$ ; after repeated distillation from metallic sodium in order to remove a stearoptene, it yields a *sesquiterpene*,  $C_{15}H_{24}$ , as a mobile, colourless oil of aromatic odour, which boils at  $256^\circ$ , and has a density of  $0.897$  at  $15.3^\circ$ , and is slightly lævotatory. This soon resinifies on exposure to air, and on adding concentrated sulphuric acid to its chloroform solution the liquid becomes first green, then blue, and red on heating.

The author concludes that the "cannabene," prepared from this essence by Personne, was a mixture.

W. J. P.

**Constitution of Isonitrosoketones.** By GIUSEPPE ODDO (*Ber.*, 1895, 28, 1915—1916).—Isonitrosocamphor, whether obtained by the method of Claisen and Manasse, by the action of sodium ethoxide and amylic nitrite on camphor (Abstr., 1889, 619), or by the author's method of treating camphorcarboxylic acid with sodium nitrite (Abstr., 1893, i, 660), behaves in most reactions in the same manner. Both products are converted into camphorquinone by nitrous acid, and into camphorimide by sulphuric acid, and with ethylic iodide the salts yield the same *ethylic* salt, melting at  $73^\circ$ , and crystallising with  $\frac{1}{2}$  mol.  $H_2O$ ; benzoic chloride also converts them into the same *benzoyl* derivative, melting at  $127$ — $128^\circ$ . Towards acetic chloride, however, the two behave in a totally different manner, the isonitrosocamphor obtained from camphorcarboxylic acid always yielding the *anhydride*,  $(C_8H_{14} \begin{smallmatrix} \text{CO} \\ | \\ \text{C:N} \end{smallmatrix})_2O$ , which melts at  $172^\circ$ , and yields a *monoxime* and a *monohydrazone*; the product obtained by Claisen and Manasse's method, on the other hand, is converted into a substance of unknown constitution melting at  $222^\circ$ , if treated directly with acetic chloride; if, on the other hand, the reaction takes place in ethereal solution it is converted into an isomeride melting at  $151^\circ$ , which dissolves readily in alkalis, and yields liquid *methylic* and *ethylic* derivatives boiling at  $270^\circ$  and  $278^\circ$  respectively. It is no longer converted by nitrous acid into camphorquinone, and has probably the constitution  $\begin{smallmatrix} \text{HN} \\ | \\ \text{O} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{C}_8\text{H}_{14} \\ | \\ \text{CO} \end{smallmatrix}$ .

This difference in the behaviour of the isonitrosocamphor obtained by different methods is probably due to the fact that the two compounds are stereoisomerides, the one obtained by the author's method being anti-nitrosocamphor, whilst Claisen's is syn-isonitrosocamphor.

H. G. C.

**Campholenic Derivatives.** By AUGUSTE BÉHAL (*Compt. rend.*, 1895, 120, 1167—1170).—The results described by Tiemann (this vol., i, 426) agree in general with those obtained by the author. The inactive amide prepared by Tiemann by boiling isoamidocam-

phor with acids, has been prepared by the author by the action of hydrochloric acid or hydriodic acid on the active amide. Tiemann's statements, that hydrochloric acid is without action on camphoroxime, and that the production of campholene when campholenic acid is heated with traces of sodium is due to the presence of campholenolactone, do not agree with the author's results (this vol., i, 240 and 241), and it would seem that Tiemann has not distinguished between the two distinct lactones described by the author (this vol., i, 552). The constitution attributed by Tiemann to the active campholenic acids is not in accordance with Guerbet's results (Abstr., 1894, i, 254), nor even with his own observations.

C. H. B.

**Pyrazolone. A Reply.** By FRIEDRICH STOLZ (*J. pr. Chem.*, 1895, [2], 52, 138—141).—The author replies to v. Rothenburg's recent statements concerning the pyrazolone controversy (this vol., i, 571).

A. G. B.

**Chlorophyll.** Part V. By EDWARD SCHUNCK (*Proc. Roy. Soc.*, 1894, 55, 351—356; compare Abstr., 1893, i, 41; 1889, 279; 1887, 972).—The author gives the results of the analyses of some of the substances previously described. Phyllocyanin cupric acetate apparently has the composition  $C_{67}H_{71}N_5O_7Cu_2$ ; pure phyllocyanin could not be obtained from this compound.

Analyses of pure phyllotaonin, methyl- and ethyl-phyllotaonin, and phyllotaonin acetate are given. Several formulæ are mentioned which agree with these analyses.

J. J. S.

**Benzylcysteine.** By F. SUTER (*Zeit. physiol. Chem.*, 1895, 20, 562—563).—*Benzylcysteine*,  $NH_2 \cdot CMe(SC_6H_5) \cdot COOH$ , is formed by the interaction of cysteine hydrochloride, benzylic chloride, and soda at ordinary temperatures. It crystallises in pearly, lustrous plates, and melts and decomposes at  $215^\circ$ . The compound reacts with alkaline copper solution like ethylcysteine (Abstr., 1892, 1111), and evolves ammonia when boiled with soda.

J. B. T.

**Pyridine produced during Coffee Roasting.** By ADOLFO MONARI and L. SCOCCIANI (*Gazzetta*, 1895, 25, i, 115—117).—On heating Mocha coffee at  $260^\circ$ , a distillate is obtained which yields an oil when treated with potassium carbonate solution; the oil consists of pyridine and a small proportion of homologues of this base. Neither ethylamine nor trimethylamine could be detected.

W. J. P.

**Synthesis of Isoquinoline Derivatives.** By PAUL FRITSCH (*Annalen*, 1895, 286, 1—26; compare Abstr., 1893, i, 366 and 427).—1 : 3-*Hydroxybenzylideneamidoacetal*,  $OH \cdot C_6H_4 \cdot CH \cdot N \cdot CH_2 \cdot CH(OEt)$ , crystallises from light petroleum in snowy needles and melts at  $71^\circ$ . 1 : 3-*Methoxybenzylideneamidoacetal*, boils at  $222^\circ$  under a pressure of 50 mm.; under the same pressure, 1 : 3-*ethoxybenzylideneamidoacetal* boils at  $228.5^\circ$ , and *piperonylideneamidoacetal* at  $238.5^\circ$ .

2-*Hydroxyisoquinoline* is obtained in a quantity approaching 80 per cent. of that required by theory when 1:3-hydroxybenzylideneamidoacetal is heated for 5 hours with a mixture of concentrated

sulphuric acid (5 parts) and water (1 part); after remaining for several hours at the ordinary temperature, the liquid is diluted with water and added to a dilute solution of sodium carbonate (compare Pomeranz, *Abstr.*, 1894, i, 552). The base crystallises from alcohol in lustrous leaflets and melts at 226–227°; it dissolves sparingly in organic solvents, but is readily soluble in acids and alkalis, although insoluble in alkali carbonates. The *hydrochloride* crystallises from alcohol in prisms, and melts at 181–190°; the *platinochloride* forms reddish-yellow needles, and melts and decomposes at 252° when rapidly heated.

*2-Methoxyisoquinoline* is prepared from 1 : 3-methoxybenzylidene-amidoacetal and sulphuric acid of the concentration already mentioned, the liquid being extracted with ether after treatment with alkali. The base melts at 49°, and boils at 194–195° under a pressure of 50 mm.; it dissolves readily in common solvents, and crystallises from light petroleum in small needles. The *hydrochloride*, which tastes bitter, crystallises from alcohol in prismatic needles, and melts at 221°; the *sulphate* crystallises from alcohol in prisms, and the *dichromate* separates from hot water in small needles. The *platinochloride* melts and decomposes at 235–236°, and crystallises in delicate needles; the *picrate* crystallises in small, lemon-yellow needles, and melts at 194–195°. The *tartrate* is obtained as a powder on treating an acetone solution of the base with tartaric acid dissolved in a mixture of acetone and alcohol; the salt separates from an aqueous or alcoholic solution in a gelatinous condition. The *methiodide* crystallises in deep yellow prisms and melts at 196–197°; the *ethiodide* forms pale yellow prisms and melts at 178–179°.

*2-Ethoxyisoquinoline* melts at 7–9°, and boils at 199° under a pressure of 50 mm., its sp. gr. is 1.0768 at 20°/4°, and its refractive power  $[n]_D = 1.6062$ , or  $M = 55.5$ . The *hydrochloride* crystallises from alcohol in slender needles, and melts at 223°; the *sulphate* forms prisms, and the *dichromate* crystallises from hot water in lustrous, yellowish-brown prisms which darken on exposure to air. The *platinochloride* separates in slender needles, and melts at 245°. The *picrate* crystallises from hot water in slender, yellow needles, and melts at 202°; the *methiodide* and *ethiodide* melt at 193–194° and 122–123° respectively.

*2:3-Methylenedioxyisoquinoline*,  $\text{CH}_2\text{O}_2\text{C}_9\text{NH}_5$ , is prepared by dissolving piperonylideneamidoacetal in sulphuric acid (5 parts) mixed with water (1 part), saturating the liquid with hydrogen chloride at 0°, and allowing it to remain in a closed vessel at this temperature for 10 days, and subsequently for four days at the ordinary temperature. The base crystallises from light petroleum, melts at 124°, and boils at 214–216° under a pressure of 50 mm., a portion becoming decomposed. The *hydrochloride* crystallises from alcohol in needles, and melts and decomposes at 250°; the *platinochloride* forms lustrous, gold-coloured needles, and melts at 243°, undergoing decomposition. The *picrate* crystallises in yellow needles, and chars when heated; the *methiodide* separates from alcohol in yellow prisms, and melts at 244°.

The foregoing quinoline derivatives, in dilute acid solution,

exhibit fluorescence, bluish-violet in the case of methoxy- and ethoxyisoquinoline, whilst solutions of methylenedioxyisoquinoline show green fluorescence; hydroxyisoquinoline exhibits bluish-violet fluorescence only in concentrated sulphuric acid solution.

Tetrahydro-derivatives have been prepared by reducing methoxyisoquinoline and ethoxyisoquinoline in alcoholic solution with sodium, and also from the methiodide and ethiodide of these compounds by means of tin and hydrochloric acid. The physical properties of the tetrahydro-derivatives, together with the melting-points of their salts, are collected in the following table:—

	B. p. (under 50 mm.).	Sp. gr. at 20°/4°.	$[\eta]_D$ at 20°.	<i>M.</i>	Hydro- chloride.	Platino- chloride.
					m. p.	m. p.
2-Methoxytetrahydroisoquinoline .....	184—186°	1·0987	1·5638	49·41	228—229°	202°
2:2'-Methoxymethyltetrahydroisoquinoline..	179°	1·0503	1·5481	53·60	201—202°	206°
2:2'-Methoxyethyltetrahydroisoquinoline....	188—189°	1·0352	1·5415	58·08	219—220°	184—185°
2-Ethoxytetrahydroisoquinoline.....	194—195°	1·0916	1·5523	51·90	256°	218°
2:2'-Ethoxymethyltetrahydroisoquinoline....	187—188°	1·0255	1·5389	58·40	196—197°	209°
2:2'-Ethoxyethyltetrahydroisoquinoline....	197—198°	1·0309	1·5417	62·63	210—211°	170—171°

2:3-Methylenedioxy-2'-methyltetrahydroisoquinoline (hydrohydrastinine) is obtained by reducing the methiodide of methylenedioxyisoquinoline in alcoholic solution with tin and hydrochloric acid; after removing the metal in the form of sulphide, the liquid is rendered alkaline and extracted with ether. It separates from light petroleum in tabular crystals and melts at 60—61°. Careful comparison of the base and its derivatives with hydrohydrastinine (Freund) and its salts establishes their identity, and the product of oxidation of methylenedioxyethyltetrahydroisoquinoline is identical in every respect with hydrastinine obtained from hydrastine.

In order to show that condensation of meta-substituted derivatives of benzylideneamidoacetal takes place in the para-position with regard to the substituent, the oxidation of 2:2'-ethoxymethyltetrahydroisoquinoline was undertaken. The action of a 3 per cent. solution of potassium permanganate in presence of alkali gives rise to an acid,  $C_{12}H_{13}NO_5 + H_2O$ , which crystallises from chloroform and melts at 100°; the barium salt has the composition  $(C_{12}H_{12}NO_5 + H_2O)_2Ba$ . Chromic acid oxidises this acid to ethoxymethylphthalimide,  $OEt \cdot C_6H_3 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NMe$ , which crystallises from alcohol in prismatic needles, and melts at 110—111°. Ethoxyphthalic acid  $[COOH : COOH : OEt = 1 : 2 : 5]$  is obtained from the foregoing substance by treating it with a boiling solution of potash (33 per cent.) for 15 minutes; it crystallises from hot water in leaflets, containing



1H<sub>2</sub>O, and becomes anhydrous at 100°, melting at 163°. If kept for some time at 220°, the substance melts at 80°. M. O. F.

**Phenylpyrroline and Pyridylpyrroline; Constitution of Nicotinic.** By AMÉ PICTET and PIERRE CRÉPIEU (Ber., 1895, 28, 1904—

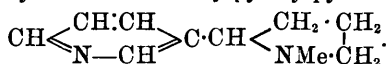
1912).—1-Phenylpyrroline,  $\begin{matrix} \text{CH:CH} \\ | \\ \text{CH:CH} \end{matrix} > \text{NPh}$ , is obtained by the distillation of normal aniline mucate, the yield being fairly good. It has all the properties described by Köttnitz (this Journal, 1873, 163), boils at 234°, is very volatile in a current of steam, and colours pine-wood violet in presence of alcohol and hydrochloric acid. When distilled through a tube heated to dull redness, it is, to a large extent, converted into an isomeric phenyl derivative, in which the latter group is combined with carbon. It can be separated from unaltered 1-phenylpyrroline by fractional crystallisation from light petroleum, in which the latter is more readily soluble. It forms nacreous plates, which become pink on exposure to air, melts at 129°, boils at 271—272° under 726 mm. pressure, volatilises in a current of steam, and sublimes in broad plates. It colours pine-wood violet, and, on oxidation, yields benzoic acid, proving that the phenyl group is combined with one of the carbon atoms; it is, as yet, uncertain whether it is a 2- or 3-phenyl derivative, although, as Ciamician and Silber (Abstr., 1887, 597) have shown that 1-acetylpyrroline under similar conditions passes into 2-acetylpyrroline, it is probable that in the case of the phenyl derivative the 2-phenylpyrroline is also formed.

1 : 3-Pyridylpyrroline,  $\text{CH} < \begin{matrix} \text{CH:CH} \\ | \\ \text{N=HC} \end{matrix} > \text{C:N} < \begin{matrix} \text{CH:CH} \\ | \\ \text{CH:CH} \end{matrix}$ , is obtained

in a similar manner to the phenyl derivative by distilling a mixture of 3-amidopyridine and mucic acid; the product contains large quantities of unaltered amidopyridine, which may be partially removed by treating the product with water; the residual oil is then boiled with acetic anhydride, and the 3-acetamidopyridine thus formed separated from the pyridylpyrroline by fractional distillation. The former crystallises in lustrous plates, melts at 131°, boils at 326—327°, and, like amidopyridine, colours pine-wood orange-yellow. 1-Pyridylpyrroline boils at 250·5—251° under 730 mm. pressure, has a sp. gr. of 1·044 at 24°/4°, and an odour somewhat resembling that of benzaldehyde; it colours pine-wood blue. The *picrate* crystallises in yellow needles, melting at 178°; the *platinochloride* in pale yellow plates, melting and decomposing at 190°; the *mercuriochloride* in long, white needles, melting at 189°; and the *methiodide* in small, white needles, melting at 241°. On heating, it undergoes intramolecular change even more readily than the phenyl derivative, yielding a *c*-phenylpyrroline, which is separated from the unaltered base by washing with light petroleum, and then dissolving the residue in benzene and precipitating with light petroleum. It forms a crystalline mass of microscopic, white needles, melting at 72°, gives an orange-red coloration with very dilute ferric chloride, and a dark blue pine-wood reaction. The *picrate* crystallises in well-developed yellow prisms, melts at 182°, and is much less soluble in

boiling water than the picrate of the 1-pyridyl derivative; the *platinochloride*,  $(C_5H_4N)_2PtCl_6 + 2H_2O$ , forms golden-yellow needles, and decomposes at  $150^\circ$  without melting; the *mercuriochloride* crystallises in small, pale yellow needles, melting at  $178$ — $179^\circ$ ; and the *methiodide* in similar crystals, melting at  $170$ — $171^\circ$ . The *potassium* derivative, obtained by the action of metallic potassium at the melting point, is a light grey, crystalline powder.

The recent investigations of Pinner and others have shown that nicotine is probably a 1 : 2 : 3-methylpyridylpyrrolidine,



By careful oxidation, nicotine loses 4 atoms of hydrogen forming nicotyrine, which, if the above constitution of nicotine be correct,

must be  $CH \begin{array}{c} \diagup CH:CH \\ \diagdown N-CH \end{array} > C \cdot C \begin{array}{c} CH \cdot CH \\ | \\ NMe \cdot CH \end{array}$ , or is the 1-methyl derivative

of the authors' synthetical pyridylpyrroline, if the pyridyl group really occupies the 2-position. When the potassium salt of the synthetical base is heated with methylic iodide, the potassium is displaced by methyl, but at the same time, it combines with methylic iodide, yielding the *methiodide* of 2 : 3-pyridylpyrroline; this crystallises in long, yellow needles, melts at  $207^\circ$ , and colours pine-wood green. A direct comparison of this substance with the methiodide obtained from nicotyrine has shown that in all probability they are identical, but to prove this definitely, it is necessary to obtain larger quantities of the synthetical compound.

H. G. C.

**Nicotine.** By ADOLF PINNER (*Ber.*, 1895, **28**, 1932—1935).—A criticism of the recent paper of Oliveri (this vol., i, 433), in which it is shown that the compounds obtained by the latter by the action of bromine on powdered nicotine hydrobromide have not the constitution assigned to them, but are in reality mixtures. The constitutional formula suggested by Oliveri, which had already been considered by the author, is quite incompatible with the recent results of the chemical and physical investigation of nicotine.

H. G. C.

**Action of some Inorganic Cyanides on Chlorocaffeine.** By M. GOMBERG (*Amer. Chem. J.*, 1895, **17**, 403—420).—The product obtained by heating bromocaffeine with an alcoholic solution of potassium cyanide is identical with that previously obtained by similar treatment of chlorocaffeine (*Abstr.*, 1893, i, 375), and is shown to be *caffeinecarboxylamide*. When heated at  $250^\circ$  with phosphoric anhydride, it yields *cyanocaffeine*,  $C_8H_7N_4O_2CN$ , which crystallises in small prisms, melts at  $151^\circ$ , and freezes at  $109$ — $110^\circ$ ; it sublimes unchanged, and dissolves in hot water, hot alcohol, methylic alcohol, chloroform, and hot benzene, but not in ether. Cyanocaffeine is only slowly converted into the amide when boiled with water or dilute alcohol, unless a little potassium cyanide is present, when the conversion is rapid and complete.

Chlorocaffeine was heated with a solution of potassium cyanide in

(1) absolute alcohol; (2) water; (3) methylic alcohol; also with mercuric cyanide in alcohol, and with potassium mercuric cyanide in alcohol; furthermore, chlorocaffeine was fused with potassium cyanide. It was found, however, that none of these methods yields so large a proportion of cyanocaffeine as that obtained by dehydrating the carboxylamide with phosphoric anhydride.

By treating cyanocaffeine with sodium in amyl alcohol, crystals of an organic base, probably caffeine-methylamine,  $C_8H_9N_4O_2 \cdot CH_2 \cdot NH_2$ , were prepared, but were not fully identified.

*Caffeinecarboxylic acid*,  $C_8H_9N_4O_2 \cdot COOH$ , may be prepared from the amide by dissolving it in sulphuric acid (1 : 1) and passing a stream of nitrous anhydride through the solution until a few drops give no immediate precipitate on the addition of water; water is then added to precipitate the carboxylic acid. It forms silky, acicular crystals of sour taste and bitter after taste, and melts and decomposes at  $225-226^\circ$ ; it dissolves in hot water and hot alcohol, but not in chloroform, carbon bisulphide, or benzene. The *sodium* salt, with  $2H_2O$ ; *potassium*, with  $2H_2O$ ; *calcium*, with  $5H_2O$ ; *barium*, with  $5H_2O$ ; *copper*, with  $4H_2O$ ; and the *silver* salt are described. The *methylic* salt melts at  $201.5^\circ$  (uncorr.), and sublimes unchanged; the *ethylic* salt melts at  $207-208^\circ$ , and also sublimes unchanged.

The author concludes by pointing out that the above compounds are the first compounds of caffeine in which the carbon of the  $CH$ -group has been linked to a new carbon atom. The ease with which caffeinecarboxylic acid loses carbonic anhydride when heated is in accord with the general nature of many acids in which the carboxyl group is attached to an unsaturated carbon atom. Thus the position of the carboxyl group is, to a certain extent, established and E. Fischer's formula for caffeine confirmed.

A. G. B.

**New Alkaloid contained in Coffee.** By PIETRO PALLADINO (*Gazzetta*, 1895, 25, i, 104-110).—The author extracts the bases from ground coffee berries by repeated boiling with milk of lime, filters, treats the liquor with lead acetate, and repeatedly extracts with chloroform to remove the caffeine. The aqueous liquor is then concentrated with the addition of sulphuric acid, and, after dilution and filtration, is precipitated with Dragendorff's reagent; a well-crystallised double *iodide* of bismuth and caffeine (Abstr., 1894, i, 214) is thus ultimately obtained.

*Caffeine hydrochloride*,  $C_{14}H_{16}N_2O_4 \cdot HCl + H_2O$ , crystallises in small, colourless needles, loses water at  $110^\circ$ , and melts at  $180^\circ$  with decomposition; it is very soluble in water, as is also the *platinochloride*,  $C_{14}H_{16}N_2O_4 \cdot H_2PtCl_6$ , which crystallises in long, red prisms.

Caffeine,  $C_{14}H_{16}N_2O_4$ , crystallises in colourless, deliquescent needles, which slowly turn red in dry air, and melt and decompose at  $140^\circ$ ; it does not sublime, has a feebly alkaline reaction, but no circular polarisation in solution. Its physiological action has not yet been fully investigated, but it seems to act as a narcotic poison.

W. J. P.

**Narceïne.** By MARTIN FREUND and HUGO MICHAELS (*Annalen*, 1895, **286**, 248—255); compare Abstr., 1894, i, 58 and 477).—*Narceïneamide*,  $C_{23}H_{26}N_2O_7 + H_2O$ , is the substance specified in D.R.P. 58,394, under the name of methylnarcotamide; it is obtained by allowing narcotine methiodide to remain in contact with alcoholic ammonia for several days. It crystallises from dilute alcohol, and contains  $1H_2O$ , which is removed at  $100^\circ$ ; the substance, when anhydrous, melts at  $78^\circ$ , and in the hydrated condition at  $125^\circ$ , becoming solid above this temperature, and finally melting at  $178^\circ$ . The *hydrochloride* melts at  $236$ — $237^\circ$ .

*Narceïneimide*,  $C_{23}H_{26}N_2O_6$ , crystallises from alcohol in small, yellow needles, and melts at  $150^\circ$ ; its *hydrochloride* melts at  $239$ — $240^\circ$ ; the *nitrate* at  $224$ — $225^\circ$ ; the *hydrogen sulphate* at  $194$ — $195^\circ$ ; and the *methiodide* at  $244$ — $245^\circ$ .

*Narceonimide*,  $C_{21}H_{19}NO_6$ , is obtained by heating the methiodide of narceonimide with 30 per cent. aqueous potash, trimethylamine being eliminated; it crystallises from glacial acetic acid in slender, yellow needles, and melts at  $177.5$ — $178.5^\circ$ . The *phenylhydrazide anhydride* of narceonic acid,  $C_{27}H_{24}N_2O_6$ , is formed when the alcoholic solution of the acid is boiled with phenylhydrazine; it crystallises from a mixture of alcohol and glacial acetic acid in white prisms, and melts at  $181$ — $182^\circ$ . The *oxime anhydride*,  $C_{21}H_{19}NO_7$ , crystallises from glacial acetic acid in needles and leaflets, and melts at  $201$ — $202^\circ$ .

*Monobromonarceonic acid*,  $C_{21}H_{19}BrO_6$ , is obtained by adding bromine (1 mol.) to narceonic acid in glacial acetic acid; it separates from alcohol in white crystals, and melts at  $171$ — $172^\circ$ .

*Tribromonarceonic acid* is formed when excess of the halogen is employed; it melts at  $231$ — $232^\circ$ . M. O. F.

**Hydrocinchonine, Hydrochlorocinchonine and Hydrochlorapocinchonine.** By OSWALD HESSE (*Ber.*, 1895, **28**, 1424—1426).—The author criticises some of the results published by Konek (this vol., i, 579). It is shown that commercial cinchonine always contains more or less hydrocinchonine, and that this is beyond doubt identical with Zorn's crystalline hydrocinchonine.

When, however, pure cinchonine is reduced with sodium amalgam, an amorphous hydrocinchonine,  $C_{19}H_{23}N_2O$ , is obtained. According to David Howard the same product can be obtained from cinchonidine, and it must therefore be a tetrahydrocinchonine. As v. Miller and Rohde (*Annalen*, **276**, 109) have shown that cinchonine has a very different molecular structure from cinchonine, it follows that this amorphous reduction product cannot be a simple hydrocinchonine.

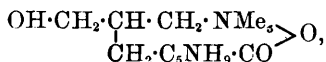
If cinchonine is heated with concentrated hydrochloric acid during 48 hours at  $85^\circ$ , or for a shorter time at  $100^\circ$ , the chief product is hydrochlorocinchonine. As this compound is not acted on by tin and hydrochloric acid, it follows that it, and not hydrocinchonine, is the chief product obtained on treating cinchonine with these reducing agents. This hydrochloro-base is identical with the hydrochlorocinchonine of Comstock and Königs (Abstr., 1887, 1124); but is not, as Konek states, identical with Zorn's chlorocinchonide and

Hesse's hydrochlorapocinchonine; Zorn's chlorocinchonide is really an additive compound formed by the addition of hydrogen chloride to apocinchonine, and is, therefore, hydrochlorapocinchonine. It is doubtful whether Konek's chlorocinchonide is hydrochlorocinchonine or hydrochlorapocinchonine. The two hydrochloro-bases may be distinguished by means of their behaviour with alcoholic potash; when treated with this reagent, hydrochlorocinchonine gives  $\alpha$ -isocinchonine, which is dextro-rotatory, whereas hydrochlorapocinchonine gives  $\beta$ -isocinchonine, which is lævo-rotatory. J. J. S.

**Action of Sodium and Amylic Alcohol on Cinchonine.** By FR. KONEK Edler VON NORWALL (*Ber.*, 1895, **28**, 1637—1641; compare this vol., i, 579).—When cinchonine is treated with sodium in boiling amyl alcoholic solution it takes up four atoms of hydrogen; and the product, when treated with potassium nitrite and sulphuric acid, yields *tetrahydrocinchonine nitrite*,  $\text{NO} \cdot \text{C}_{19}\text{H}_{25}\text{N}_2\text{O} \cdot \text{HNO}_2$ , which crystallises in silky, yellow needles. The free base instantaneously yields a colourless additive compound with methylic iodide, from which fact the deduction is drawn that the four hydrogen atoms attach themselves to the quinoline ring, that nitrogen atom remaining unaffected which, in cinchonine itself, readily takes up methylic iodide, &c., to form colourless derivatives. C. F. B.

**Constitution of Aconitine. A Reply.**—By WYNDHAM R. DUNSTAN and FRANCIS H. CARR (*Ber.*, 1895, **28**, 1379—1382).—A reply to Freund's criticisms (*Ber.*, 1895, **28**, 192) on the authors' work. J. J. S.

**Chrysanthemine.** By FRANCESCO MARINO-ZUCO (*Gazzetta*, 1895, **25**, i, 255—262).—On heating chrysanthemine at 150—160° with concentrated hydriodic acid, decomposition suddenly occurs and methylic and ethylic iodides distil over; the residue in the retort contains no chrysanthemine, but on dissolving it in water, decolorising with sulphurous acid, and adding potassium bismuth iodide solution, tetramethylammonium bismuthiodide separates. From the mother-liquor, after precipitating the bismuth and iodine, a *methylypiperidine-carboxylic acid*,  $\text{C}_5\text{NH}_9\text{Me} \cdot \text{COOH}$ , may be separated as its *aurochloride*,  $\text{C}_7\text{H}_{13}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , which crystallises in hard yellow prisms melting at 130°; the acid itself is a syrupy liquid which ultimately solidifies to a hygroscopic crystalline mass. This decomposition of the alkaloid supports the constitution previously assigned to chrysanthemine by the author (*Abstr.*, 1892, 84) but in view of the optical inactivity of the alkaloid he considers that the constitution



is the more probable.

W. J. P.

**The Alkaloids of Cannabis Indica and Cannabis Sativa.** By FRANCESCO MARINO-ZUCO and G. VIGNOLO (*Gazzetta*, 1895, **25**, i, 262—268).—Various parts of the common hemp (*Cannabis sativa*) and of the Indian hemp (*Cannabis indica*) were exhaustively

extracted by boiling with water acidified with sulphuric acid, and the extract evaporated until it acquired a syrupy consistency, any inorganic salts being removed as they separated. It was then diluted with water, decolorised with animal charcoal, treated with soda, and precipitated with potassium bismuth iodide, the double salt deposited being subsequently converted into the *hydrochloride* of the alkaloid in the usual way. The salt obtained from both varieties of *Cannabis* forms a colourless, crystalline, deliquescent mass; that from *Cannabis sativa* is physiologically almost inactive, but gives rise in the frog to temporary cardiac depression; the hydrochloride from *Cannabis indica* is, however, highly toxic and causes far greater depression of cardiac activity than the preceding. W. J. P.

**Scopoleïne.** By W. LUBOLDT (*Chem. Centr.*, 1895, i, 61; from *Apoth. Zeit.*, 1894, 9, 869).—Salicylscopoleine is best prepared by Liebermann and Limpach's method of heating scopolin with salicylide at  $230^{\circ}$ , and extracting the base with dilute hydrochloric acid; it crystallises in white needles melting at  $105^{\circ}$ . The hydrochloride, hydrobromide, sulphate, and aurochloride are described. The *platinochloride* crystallises with  $2\text{H}_2\text{O}$  in orange leaflets melting at  $205^{\circ}$  and with  $1\text{H}_2\text{O}$  in red needles melting at  $212^{\circ}$ ; numerous analyses show that the base has the composition  $\text{C}_{15}\text{H}_{17}\text{NO}_4$ . The *acetyl* and *benzoyl* derivatives of scopoleine are described. W. J. P.

**Senecionine and Senecine.** By ALEXANDRE GRANDVAL and HENRI LAJOUX (*Compt. rend.*, 1895, 120, 1120—1123).—*Senecio vulgaris* contains small quantities of two alkaloids, which the authors call senecionine and senecine. Both are precipitated by mercuric potassium iodide, and both crystallise readily from chloroform, in which they are easily soluble; senecionine, however, is less soluble in alcohol than senecine, and is only very slightly soluble in ether, which dissolves senecine readily.

*Senecionine*,  $\text{C}_{18}\text{H}_{26}\text{NO}_6$ , crystallises in small, rhomboidal tables; it has a feebly bitter taste, and a strongly alkaline reaction, neutralising acids with formation of salts, which do not crystallise readily. Its rotatory power is  $[\alpha]_D = -80.49^{\circ}$ . With a mixture of ferric chloride and potassium ferricyanide, it yields a precipitate of Prussian blue, and with acidified potassium permanganate, it gives a violet coloration.

*Senecine* has a very much bitterer taste than senecionine. It crystallises from ether in silky tufts, and forms a hydrogen tartrate, which crystallises readily from water in efflorescent needles. No crystalline hydrogen tartrate of senecionine could be obtained. Senecine yields a precipitate of Prussian blue with a mixture of ferric chloride and potassium ferricyanide, and a violet coloration with acidified potassium permanganate. With sulphuric acid, a yellowish coloration, changing to reddish-brown with a violet tint is obtained; with nitric acid, a violet-red coloration, and a deep violet precipitate; with sulphovanadic acid, a violet-brown coloration.

C. H. B.

## Organic Chemistry.

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**Solubility of Iodoform in Alcohol and Ether.** By GUSTAV VULPIUS (*Zeit. anal. Chem.*, 1895, **34**, 465; from *Pharm. Centralhalle*, [2], **14**, 117).—At 17—18°, 1 part of iodoform dissolves in 67 parts of alcohol (of 90·5 vols. per cent.) or in 5·6 parts of ether. At the boiling point, 9 parts of alcohol dissolve 1 part of iodoform. The three forms in which iodoform comes into commerce differ only in the rate at which they dissolve. The statements in the German Pharmacopœia are not quite correct. M. J. S.

**Action of Nitric acid on Saturated Hydrocarbons and their Derivatives.** By MICHAËL KONOVALOFF (*Ber.*, 1895, **28**, 1852—1865; compare *Abstr.*, 1894, i, 265, 277).—Diisobutyl is converted by dilute nitric acid at 105—110° into a mixture of nitro-compounds, which chiefly consist of *tertiary nitrodiisobutyl*,  $\text{NO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$ . This is a yellowish liquid, which boils at 201—202°, has the sp. gr. 0·9396 at 0/0°, and the molecular refraction 44·76. The corresponding *amine* boils at 145°, and forms a *hydrochloride*, which crystallises in tablets or thin needles, melting at 157—160°. When the nitro-compound is further heated with dilute nitric acid at 120—125°, *dinitrodiisobutyl*,  $\text{C}_8\text{H}_{16}(\text{NO}_2)_2$ , which is also a tertiary compound, is formed; it crystallises in colourless plates, and melts at 124—125°. The *diamine* is a strong fuming base, which absorbs carbonic anhydride from the air and yields crystalline salts.

*Dinitrodiisopropyl*, which is formed in small quantity in the nitration of diisopropyl, is also a crystalline substance, and melts at 206—208°.

Diisoamyl is also mainly converted into a tertiary nitro-compound by dilute nitric acid. *Nitrodiisoamyl* boils at 125° (pressure = 22·5 mm.), but decomposes when distilled under the atmospheric pressure. It is easily reduced to an *amine*, which boils at 190°.

Nitroisopropylbenzene, which had previously been obtained by the action of dilute nitric acid on isopropylbenzene, boils at 125—127° (pressure = 15 mm.) when pure, and has the sp. gr. 1·1176 at 0/0°. Normal butylbenzene is converted into a *secondary nitrobutylbenzene*,  $\text{NO}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , by dilute nitric acid; this boils at 151—152° (pressure = 25 mm.), and has the sp. gr. 1·0756 at 0/0°, and the molecular refraction 50·33. When its potassium derivative is treated with bromine, a *monobromide* is formed which melts at 55—56°. The corresponding *amine* boils at 220—220·5°, and yields crystalline salts. *Nitroisobutylbenzene*,  $\text{NO}_2\cdot\text{CHPh}\cdot\text{CHMe}_2$ , is obtained in a similar manner to the foregoing compound; it boils at 145—146° (pressure = 25 mm.). The *monobromide* is an oily liquid; the *amine* boils at 213·5—215°, and yields crystalline salts; the *hydrochloride* melts at 275—277°, the *picrate* at 166—168°, and the *oxalate* at 120·5—122°. The *sodium derivative of the nitro-compound* has the

formula  $\text{NO}_2 \cdot \text{CPhNa} \cdot \text{CHMe}_2$ , and gives characteristic reactions with salts of iron, copper, &c.

Tertiary butylbenzene also yields a nitro-compound, which has not yet been obtained pure.

*Nitrodibenzyl*,  $\text{NO}_2 \cdot \text{CHPh} \cdot \text{CH}_2\text{Ph}$ , obtained in a similar manner, volatiles slowly with steam. The *hydrochloride* of the *amine* melts at  $251.5-252.5^\circ$ .

Toluene when heated at  $100^\circ$  with nitric acid of sp. gr. 1.12 is converted into phenylnitromethane, a yield of 50 per cent. being obtained. This substance is converted by reduction into benzylamine. Mesitylene is readily nitrated by nitric acid of sp. gr. 1.155 at  $100^\circ$ , and yields *xylylnitromethane*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{CH}_2\text{NO}_2$ , which crystallises in thick, four-sided prisms, melting at  $46-47^\circ$ . It is only slowly dissolved by alkalis. The *amine* boils at  $220-221^\circ$ , and its *hydrochloride* melts at  $245-246^\circ$ .

The facts here recorded confirm the conclusions previously drawn by the author from his experiments on nitration.

The nitro-compounds are best obtained from their metallic derivatives by the action of hydrogen sulphide, boric acid, or carbonic anhydride.

The reduction of the nitro-compounds described above always gives rise to the production of a small quantity of a neutral substance, probably an aldehyde, ketone, or alcohol, in addition to the amine.

A. H.

**Reaction for Primary and Secondary Nitro-compounds.** By MICHAËL KONOVALOFF (*Ber.*, 1895, **28**, 1850—1852).—The reaction with nitrous acid (V. Meyer) is not well shown by nitro-compounds containing more than six carbon atoms; on the other hand, such compounds may readily be detected in the following manner. The substance to be tested is shaken with a little concentrated aqueous potash or sodium ethoxide, and the resulting salt extracted with a little water; the aqueous solution is then placed in a tube along with a small volume of ether or benzene, and ferric chloride added drop by drop, the tube being well shaken after the addition of each drop. A red coloration indicates the presence of a primary or secondary nitro-compound; this coloration is due to the formation of a ferric salt, and it is found that the solubility of the ferric salt in ether, benzene, &c., increases with the molecular weight of the nitro-compound. This reaction is very delicate, and is not given by nitrites.

A. H.

**Reactions of Aluminium Amalgam.** By HANS WISLICENUS and LUDWIG KAUFMANN (*Ber.*, 1895, **28**, 1983—1986).—The first portion of this paper is a reply to the claims of priority of Radziejewski (this vol., i, 412) and of Cohen and Ormandy (this vol., ii, 394). In the second portion, it is shown that under certain circumstances aluminium amalgam brings about reduction, even if all traces of water are excluded. Thus nitro-compounds, and all alkylic nitrites and nitrates, are reduced when treated with aluminium amalgam and absolute alcohol from which all traces of water have been removed by previous treatment with aluminium amalgam; the



product contains hydroxylamine derivatives, and also combined aluminium, which separates out as hydroxide on the addition of water.  
H. G. C.

**Removal of Phosphine from Acetylene prepared from Calcium Carbide. Compound of Silver Acetylide with Silver Nitrate. Preparation of Iodinium Compounds.** By CONRAD WILLGERODT (*Ber.*, 1895, **28**, 2107—2115).—Acetylene, prepared by the action of water on calcium carbide, contains phosphine, which can be detected by passing the gas through silver nitrate solution. The white precipitate produced by the acetylene is coloured dark by silver phosphide, whilst phosphoric acid passes into solution. The phosphine may be completely removed by passing the gas through bromine water.

The compound of silver nitrate with silver acetylide can be prepared in a pure state by passing purified acetylene into aqueous silver nitrate; it is a white mass, which can be preserved in the dark for a long time. The temperature of explosion of the compound is about  $230^{\circ}$ .

When the aromatic iodosochlorides are treated with the compound of silver chloride and silver acetylide, free from silver phosphide, and suspended in water, the chlorides of dialkyliodinium bases are formed. The reactions which occur, for example, when phenylic iodosochloride is used are the following.

- (1.)  $\text{PhICl}_2 + \text{HC}\equiv\text{C}\cdot\text{Ag}, \text{AgCl} = \text{CH}\equiv\text{C}\cdot\text{IPhCl} + 2\text{AgCl}.$
- (2.)  $\text{PhICl}_2 + \text{H}_2\text{O} = \text{PhIO} + 2\text{HCl}.$
- (3.)  $\text{CH}\equiv\text{C}\cdot\text{IPhCl} + 2\text{HCl} = \text{C}_2\text{H}_3\text{Cl}_2\cdot\text{IPhCl}.$

*Dichlorethylphenyliodinium chloride*,  $\text{C}_2\text{H}_3\text{Cl}_2\cdot\text{IPhCl}$ , crystallises in colourless prisms and decomposes at  $178\text{--}179^{\circ}$ . *Dichlorethylparatolyliodinium chloride* crystallises in long needles or prisms, which decompose at  $178\text{--}179^{\circ}$ . Both of these chlorides form platinochlorides.

The nitrates of these bases can be obtained by the action of the chlorides on silver nitrate, or by the action of the iodosochloride on the compound of silver acetylide with silver nitrate. In the latter case, when phenylic iodosochloride is used, *chlorovinylphenyliodinium nitrate*,  $\text{C}_2\text{H}_2\text{Cl}\cdot\text{IPh}\cdot\text{NO}_3$ , is obtained. This substance crystallises in prisms and decomposes at  $150\text{--}153^{\circ}$ .

*Ethenylphenyliodinium nitrate*,  $\text{C}_2\text{H}_3\cdot\text{IPhCl}$ , is probably formed as a crystalline mass when phenyl iodosochloride acts on the compound of silver acetylide with silver nitrate suspended in chloroform. *Dichlorethylphenyliodinium nitrate* decomposes at  $162^{\circ}$ .

*Dichlorethylphenyliodinium iodide* forms needles which melt and decompose at  $108^{\circ}$ .  
A. H.

**Acetylene and its Hydrate.** By P. VILLARD (*Compt. rend.*, 1895, **120**, 1262—1265).—Acetylene, purified in the same way as nitrous oxide (*Abstr.*, 1894, ii, 379), solidifies when the liquefied gas is allowed to evaporate under atmospheric pressure; the solid melts at  $-81^{\circ}$ ,

and the boiling point of the liquid is  $-83^{\circ}$ . Its vapour pressure, in atmospheres, is as follows:—

$t$ ....	$-90^{\circ}$	$-85^{\circ}$	$-81^{\circ}$	$-70^{\circ}$	$-60^{\circ}$	$-50^{\circ}$	$-40^{\circ}$
$p$ ....	0.69	1.00	1.25	2.22	3.55	5.3	7.7
$t$ ....	$-23.8^{\circ}$	$0^{\circ}$	$5.8^{\circ}$	$11.5^{\circ}$	$15.0^{\circ}$	$20.2^{\circ}$	
$p$ ....	13.2	26.05	30.3	34.8	37.9	42.8	

These values are somewhat higher than those given by Ansdell, but concordant results were obtained with different specimens of the gas and with different fractions of the liquefied gas. It is probable that Ansdell's acetylene contained a small quantity of chlorethylene.

Acetylene crystals have no action on polarised light. The coefficient of solubility of the gas at  $0^{\circ}$  under a pressure of 4.65 atmos. is 1.6.

Acetylene hydrate forms under the same conditions as the hydrates of nitrous oxide (Abstr., 1894, ii, 278) or carbonic anhydride (this vol., ii, 44); its crystals have no action on polarised light. Its vapour pressure is as follows:—

$t$ .....	$0^{\circ}$	$4.6^{\circ}$	$7.0^{\circ}$	$9.6^{\circ}$	$15.0^{\circ}$
$p$ .....	5.75	9.4	12.0	16.4	33.0

At  $16^{\circ}$ , the pressure is equal to that of the moist liquefied gas. Acetylene does not combine with ice, and the hydrate is practically stable below  $-0.5^{\circ}$  under ordinary pressure (?). The hydrate has the composition  $C_2H_2, 6H_2O$ , and its heat of formation is  $+15.4$  Cal. (Compare *loc. cit.*)

C. H. B.

**Combination of Nitriles with Aluminium Chloride.** By G. PERRIER (*Compt. rend.*, 1895, 120, 1423—1426).—Hydrocyanic acid, acetonitrile and propionitrile dissolve aluminium chloride with development of heat, yielding crystalline compounds of the general composition  $Al_2Cl_6, 4X$ . If the combination takes place in presence of carbon bisulphide, the products have the composition  $Al_2Cl_6, 2X$ . They are insoluble in carbon bisulphide, carbon tetrachloride and light petroleum, and are rapidly decomposed by moist air and by water with liberation of the nitrile and aluminium chloride.

$Al_2Cl_6, 4CH_3 \cdot CN$  melts at  $50-55^{\circ}$  and decomposes at about  $60^{\circ}$ ;  $Al_2Cl_6, 2CH_3 \cdot CN$  melts at  $104-105^{\circ}$  and decomposes at about  $110^{\circ}$ .  $Al_2Cl_6, 4C_2H_5 \cdot CN$  crystallises in hexagonal tables which melt at  $58-60^{\circ}$ , and the liquid decomposes at about  $80^{\circ}$ ;  $Al_2Cl_6, 2C_2H_5 \cdot CN$  crystallises in slender needles which melt at  $70-80^{\circ}$ .

When the acetonitrile and propionitrile compounds are heated, some of the nitrile is given off and at about  $360^{\circ}$  a limpid liquid distils over and solidifies to crystals of the composition  $Al_2Cl_6, CH_3 \cdot CN$ , or  $Al_2Cl_6, C_2H_5 \cdot CN$ , as the case may be. The former melts at  $145-149^{\circ}$ , and the latter at  $95^{\circ}$ ; both are decomposed by water into aluminium chloride and the nitrile.

Benzonitrile, under similar conditions, yields the compounds  $Al_2Cl_6, 4C_6H_5 \cdot CN$  melting at  $75^{\circ}$ ,  $Al_2Cl_6, 2C_6H_5 \cdot CN$  melting at  $85^{\circ}$  and

$\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_5\text{CN}$  melting at  $103\text{--}105^\circ$ . In solubility and general properties, they closely resemble the corresponding compounds in the acetic series.

When dry cyanogen is passed over gently heated aluminium chloride, a brown liquid product is formed with considerable development of heat. It crystallises on cooling and is violently decomposed by water. A similar product seems to be formed in presence of carbon bisulphide.

It seems probable that compounds similar to those described in this paper are formed as intermediate products in Desgrez's process for the preparation of nitriles by the direct combination of cyanogen with hydrocarbons of the benzene series.

Liquid cyanogen chloride seems to form no combination with aluminium chloride, but a supersaturated solution is produced, and when it solidifies the heat developed causes explosive decomposition of the whole mass, with production of solid cyanogen chloride.

C. H. B.

**Action of Halogens on Methylic Alcohol.** By ANDRÉ BROCHET (*Compt. rend.*, 1895, 121, 130—133).—Chlorine attacks methylic alcohol more readily the higher the proportion of water present. The action of the moist gas on the alcohol of  $99.5^\circ$  in diffused daylight yields mainly formaldehyde. Most probably the primary product is chloromethylic alcohol,  $\text{CH}_2\text{Cl}\cdot\text{OH}$ , which in presence of hydrochloric acid is converted into symmetrical dichloromethylic ether  $(\text{CH}_2\text{Cl})_2\text{O}$ . The latter in fact separates as an oily liquid and can be isolated; in presence of water, however, it readily decomposes into hydrogen chloride and formaldehyde. During the action of the chlorine, carbonic anhydride and carbonic oxide mixed with a small quantity of methylic chloride are continuously evolved. The carbon oxides may result from the action of the water on carbonic chloride and the monochloride  $\text{CHOCl}$ , or from the dehydrating action of the chlorine on the formaldehyde.

If the methylic alcohol is heated, methylal is obtained together with large quantities of methylic chloride, carbonic anhydride, and carbonic oxide, the action being accompanied by flame and by explosions, even in very diffused light.

Bromine in presence of sunlight has practically no action on methylic alcohol at the ordinary temperature; at  $100^\circ$ , the action is slight; at  $130\text{--}150^\circ$ , the action is somewhat energetic, the chief product being methylic bromide mixed with some carbonic anhydride, and with small quantities of carbonic oxide and formic acid if the bromine is not in excess.

Iodine at  $180\text{--}200^\circ$  attacks the alcohol with difficulty, and small quantities of carbonic anhydride, hydrogen iodide, and methylic iodide are formed. A large proportion of the alcohol is, however, converted into methylic ether, and this compound can readily be prepared by heating the alcohol in sealed tubes with 5 per cent. of iodine.

C. H. B.

**Nitro-Alcohols.** By LOUIS HENRY (*Compt. rend.*, 1895, 120, 1265—1268).—Aldehyde and nitromethane dissolve in one another

without any interaction, but in presence of water and a small quantity of potassium carbonate, an action takes place with considerable development of heat and nitroisopropyl alcohol is obtained; in presence of potassium hydroxide the action is violent. Under similar conditions, formaldehyde yields a solid product, and propaldehyde yields secondary nitrobutyl alcohol. Isobutaldehyde reacts somewhat less readily and only in presence of potassium hydroxide. Acetone and nitromethane do not react even in presence of potassium hydroxide.

*Nitroisopropyl alcohol* is a colourless, limpid, almost odourless liquid, with a very peculiar disagreeable taste. In a mixture of solid carbonic anhydride and ether, it forms a transparent, amorphous mass which after a time becomes crystalline, and melts at about  $-20^{\circ}$ ; sp. gr. = 1.1910 at  $18^{\circ}$ ; boiling point  $112^{\circ}$  under a pressure of 30 mm.; vapour density 3.58. The *acetate*,  $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NO}_2$ , is a colourless liquid, insoluble in water and boiling at about the same temperature as the alcohol itself; sp. gr. = 1.1670 at  $15^{\circ}$ . The *chloride*,  $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{NO}_2$ , obtained by the action of phosphorus pentachloride, is a colourless liquid which boils at  $172^{\circ}$  under ordinary pressure; sp. gr. = 1.2361 at  $15^{\circ}$ ; vapour density 4.23. The *nitro-alcohol*, like nitromethane, burns with a greenish-yellow flame; with excess of potash, its nitrolic derivative gives the red coloration characteristic of the group  $\text{CH}_2\cdot\text{NO}_2$ . *Secondary nitrobutyl alcohol* has similar properties.

The product of the reaction between nitromethane and formaldehyde is a crystalline solid which melts at about  $140^{\circ}$ , and dissolves in water and most organic solvents, but is only slightly soluble in ether. It may be nitroethyl ether  $(\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$ .

Having regard to the differences of composition between  $\text{HCHO}$ ,  $\text{CH}_3\cdot\text{CHO}$ , and  $\text{COMe}_2$ , and their different behaviour with respect to nitromethane, it would seem that the tendency of the latter to form additive products is conditioned by the presence of hydrogen in union with carbon in the group  $\text{CHO}$ . Since all nitroparaffins in which hydrogen is united with the same carbon atom as the  $\text{NO}_2$  group are basic like nitromethane, it would follow that all derivatives of this class containing the group,  $\cdot\text{CH}_2\cdot\text{NO}_2$ , or  $\cdot\text{CH}\cdot\text{NO}_2$ , should form additive products with aldehydes, but this conclusion has not yet been verified. The same power should also characterise nitro-alcohols which contain either of the groups specified, and as a matter of fact nitroisopropyl alcohol combines readily with formaldehyde or acetaldehyde.

The combining power, with respect to aldehydes, of nitromethane and hydrogen cyanide is as 3 to 1. In nitromethane, as in ammonia, the reaction capacity diminishes in proportion to the displacement of the hydrogen atoms by alkyl radicles.

There is some evidence that in the reaction of nitromethane with aldehydes, more than one product is formed, and not a single product only as in the action between the aldehydes and hydrogen cyanide.

C. H. B.

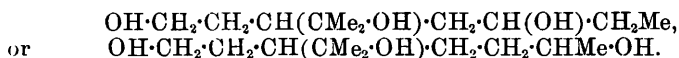
**Allylphosphoric acid.** By J. CAVALIER (*Compt. rend.*, 1895, **121**, 69—71).—Glacial phosphoric acid dissolves in allylic alcohol with

development of heat, and, after being kept at about  $100^{\circ}$  for some time, a small quantity of allylphosphoric acid is formed. The best results are obtained by gradually adding phosphoric anhydride to a well-cooled solution of allylic alcohol in its own volume of dry ether. After distilling off part of the ether and adding water, the liquid separates into two layers, the upper of which seems to contain triallylic phosphate, whilst the lower contains allylphosphoric acid, which is isolated by converting it into the barium salt and decomposing the latter with sulphuric acid.

*Allylphosphoric acid*,  $C_3H_5 \cdot H_2PO_4$ , is a syrupy, uncrystallisable, dibasic acid, which is neutral to methyl-orange when mixed with one equivalent of alkali, and to phenolphthaleïn when mixed with two equivalents. Many of its metallic salts are described; all the normal allylphosphates which are only slightly soluble in water dissolve readily in dilute acids, and are converted into the hydrogen salts. Most of the salts crystallise readily. C. H. B.

**Conversion of d- and l-Linaloöl and of Geraniol into Terpin Hydrate.** By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1895, **28**, 2137—2140).—If *d*- or *l*-linaloöl is shaken with 20 times its weight of 5 per cent. sulphuric acid for several days at the ordinary temperature, it slowly dissolves, and ether extracts an almost theoretical quantity of inactive terpin hydrate (m. p.  $117-118^{\circ}$ ) from the solution. No intermediate product of hydrolysis was isolated.

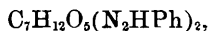
Geraniol, also, when treated in a similar manner, yields terpin hydrate, mixed, however, with a small quantity of some syrupy substance. It is thought that these facts point to the constitution,  $OH \cdot CMe_2 \cdot [CH_2]_3 \cdot CMe(OH) \cdot CH_2 \cdot CH_2 \cdot OH$ , for terpin hydrate. Pinene yields terpin hydrate even more readily when treated with dilute acids, and if Tiemann's formula for pinene is correct, then terpin hydrate would probably be



The authors consider that one of the last two formulæ is the more probable, and that terpin, which is inactive, is an intermediate product in the conversion of linaloöl into terpin hydrate. In any case it is thought that terpin hydrate is a saturated open chain compound.

J. J. S.

**Volemite, a New Heptitol.** By EMIL FISCHER (*Ber.*, 1895, **28**, 1973—1974).—Bourquelot described (*Bull. Soc. Mycol. de France*, v) under the name of *volemite*, a substance which he obtained from the fungus *Lactarius volemus*, and thought to be isomeric with mannitol. He has lately sent a specimen to the author, who finds it to be in reality a heptitol,  $C_7H_{16}O_7$ . It begins to liquefy at  $147^{\circ}$ , and melts at  $149-151^{\circ}$  (corr.  $151-153^{\circ}$ ); its specific rotation  $[\alpha]_D = +1.92$  at  $20^{\circ}$ , and it is oxidised by nitric acid, or by bromine and sodium carbonate, to a sugar *volemose*, the yellow *osazone* of which,



melts and decomposes at  $196^{\circ}$  when heated quickly. The sugar itself was not obtained crystalline.  
C. F. B.

**Ammonia Derivative of d-Glucose.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 98—105).—*d*-Glucosamine,  $C_6H_{13}NO_5$ , the molecular weight of which was determined by the cryoscopic method, separates in calculus-like aggregates of small, white needles when a solution of *d*-glucose in methylic alcoholic ammonia is kept for some weeks. The yield is about 50 per cent. of the theoretical. The pure substance, after recrystallisation from methylic alcohol, melts at  $127$ — $128^{\circ}$ , at the same time decomposing. It is not an aldehyde-ammonia, as stated by Stone (this vol., i, 320), whose analytical results are erroneous, but an isomeride of chitosamine (glucosamine), isoglucosamine, and acrosamine; its basic properties, however, are feeble than those of the last, as it does not form an oxalate. The specific rotatory power in aqueous solution is  $[\alpha]_D = +19.5^{\circ}$ . *d*-Glucosamine is slowly hydrolysed by water into its proximate constituents, and, when exposed to air, absorbs water and loses ammonia.  
JN. W.

**Discoloration and Coagulation of Milk by Heat.** By PAUL CAZENEUVE and HADDON (*Compt. rend.*, 1895, **120**, 1272—1273).—Milk which has been heated at  $130^{\circ}$  for an hour coagulates, and becomes very acid; it contains formic acid. A solution of lactose (5:100) containing a small quantity of sodium carbonate or disodium hydrogen phosphate also becomes yellow, and contains formic acid if heated for an hour at  $130^{\circ}$ . Formic acid is likewise produced when fresh milk, or the alkaline solution of lactose, is boiled for some time under atmospheric pressure, or when the alkaline lactose solution is heated on a water bath. Casein, on the other hand, when heated in sealed tubes at  $130^{\circ}$  with water containing sodium hydroxide or carbonate, or disodium hydrogen phosphate, undergoes no change.

It follows that the discoloration and coagulation of milk by heat is due to the oxidation of the lactose in presence of the alkaline salts of the milk, one product of the oxidation being formic acid, which precipitates the casein, but the latter undergoes no change, except that it is coloured yellow by the products of the decomposition of the lactose.

C. H. B.

**Origin of Unsaturated Compounds in Plants.** By CHARLES F. CROSS, EDWARD J. BEVAN, and CLAUD SMITH (*Ber.*, 1895, **28**, 1940—1945).—When barley straw was distilled with dilute sulphuric acid, furfuraldehyde and volatile acids, chiefly acetic acid, passed over. The water, as it distilled over, was replaced by means of an automatic arrangement; under these circumstances, and with acid of from 10 to 20 per cent. strength, it was found that furfuraldehyde and acetic acid were formed at about the same rate, and are consequently products of the same reaction. No such relation was apparent when the strength of the acid was 30 to 50 per cent. Various celluloses were treated in the same way, and were found to yield volatile acids in addition to varying quantities of furfuraldehyde; in all these cases, however, formic acid formed by far the larger part of the

volatile acids. Since woody matter yields a considerable amount of acetic acid when hydrolysed, whereas cellulose yields but little, it seems that the group  $\text{CH}:\text{CH}$  is present in the former, and this group may have been introduced in the process of lignification, possibly through condensation of an aldehyde group with an acetic acid residue.

C. F. B.

**Action of Formaldehyde on Amines.** By R. CAMBIER and ANDRÉ BROCHET (*Bull. Soc. Chim.*, [3], 13, 392—418).—When formaldehyde and aqueous ammonia are mixed at  $-20^\circ$ , no hexamethylenetetramine is formed, as the product remains liquid; and on removing the excess of water by means of potassium carbonate, a viscous liquid is obtained, which is at once converted into the tetramine by heat, or by the addition of caustic soda. The viscous product probably contains formaldehyde ammonia,  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}_2$ , as a small amount of a pyridine base is formed during its conversion into the tetramine.

Hexamethylenetetramine can be sublimed unchanged under very low pressure, and is not affected by water or aqueous ammonia at  $150^\circ$ , but in presence of formaldehyde it is hydrolysed by water at that temperature into methylamine and carbonic anhydride. It dissolves more easily in cold than in hot water, and forms several hydrates. The *hexahydrate*,  $\text{C}_6\text{H}_{12}\text{N}_4\cdot 6\text{H}_2\text{O}$ , forms very large, transparent, hexagonal prisms, and melts and decomposes at  $135^\circ$ . The so-called nitrosopentamethylenetetramine, formed by the action of nitrous acid on hexamethylenetetramine (Delépine, this vol., i, 326), is identical with nitrosotrimethylenetriamine. Hexamethylenetetramine and its salts are decomposed by acids quantitatively into methylamine and carbonic anhydride (compare Delépine, *loc. cit.*); it is a monacid base, perhaps feebly diacid, as it forms both normal and acid salts with the inorganic acids. The *sulphates*,  $2\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{SO}_4$ , and  $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{SO}_4$ , are both acid to phenolphthaleïn, but the former is neutral to methyl-orange; the latter is readily hydrolysed by water and alcohol into its proximate constituents, the formaldehyde in the latter case combining further with the alcohol to form ethylal. The *normal hydrochloride*,  $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{HCl}$ , is neutral to methyl-orange and acid to litmus and phenolphthaleïn; but the *acid hydrochloride*,  $\text{C}_6\text{H}_{12}\text{N}_4\cdot 2\text{HCl}$ , is acid to all three indicators; as, however, it yields the platinochloride of the normal salt, it is a molecular compound. The normal and acid *nitrates* are similar. All the above salts decompose at their melting points. The *dichromate*,  $2\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{Cr}_2\text{O}_7$ , and *tetrachromate*,  $2\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{Cr}_4\text{O}_{13}$ , explode when struck or heated.

Formaldehyde condenses with hydroxylamine hydrochloride in cold, aqueous solution to formaldoxime,  $\text{CH}_2\cdot\text{N}\cdot\text{OH}$ , or its polymeride, trioximidomethylene,  $(\text{CH}_2\cdot\text{N}\cdot\text{OH})_3$ , with liberation of an equivalent of hydrogen chloride; when the solution is heated, however, the product loses water, and hydrogen cyanide is disengaged.

Formaldehyde condenses with methylamine hydrochloride to form *trimethyltrimethylenetriamine*,  $\text{C}_9\text{H}_{18}\text{N}_6$ , an oily liquid boiling at  $166^\circ$ , the molecular weight of which was determined by the cryoscopic method. This amine is a tertiary base, whose salts are extremely soluble. It combines readily with alkylic iodides to form crystalline

additive compounds, but it does not form a nitroso-derivative, or condense with formaldehyde. The *hydrochloride*, obtained by passing dry hydrogen chloride into its benzene solution, is extremely deliquescent, and melts and decomposes at  $120^{\circ}$ . A *platinochloride* was prepared.

Formaldehyde condenses with ammonium chloride in a very complex manner. It is probable that trimethylenetriamine occurs as an intermediate product, together with its condensation products with formaldehyde, and those of the aldehyde with methylamine and dimethylamine, but under certain conditions these products act further with formaldehyde to form carbonic anhydride, methylamine, and trimethylamine. The yields of the amines are quantitative, the former or the latter being produced accordingly as the ammonium chloride or the formaldehyde is in excess. These reactions afford new and extremely convenient methods of preparing the two amines.

Formaldehyde reacts with ammonium carbonate to form hexamethylenetetramine, and with ammonium cyanide to form methylene-amidoacetonitrile.

The authors confirm v. Miller and Plöchl's formula,  $(NPh \cdot CH_2)_3$ , for the condensation product of formaldehyde with aniline. It is highly probable that the trimethylene bases are ring compounds related to the isocyanuric derivatives, and having constitutions such as  $NMe \langle \begin{smallmatrix} CH_2 \cdot NMe \\ CH_2 \cdot NMe \end{smallmatrix} \rangle CH_2$ . The parent substance, trimethylenetriamine, is thus a secondary base, forming nitroso-derivatives, and condensing with formaldehyde. The alkylic derivatives are tertiary bases, and therefore do not form nitroso- or condensation products, but, on the other hand, readily form alkylic iodides.

Triphenyltrimethylenetriamine is readily oxidised by dilute potassium permanganate, or even by air, to phenylic isocyanide, and is broken up by hydrogen cyanide, with formation of phenylamidoacetonitrile,  $NHPh \cdot CH_2 \cdot CN$ ; similarly amidoacetonitrile, or its condensation product with formaldehyde, is obtained from a mixture of formaldehyde and the latter substance.

JN. W.

### Action of Alkali Sulphites on Fatty Diazo-compounds.

By HANS V. PECHMANN (*Ber.*, 1895, 28, 1847—1850).—Ethylic diazoacetate unites with potassium sulphite to form *potassium ethylic sulphohydrazimethylenecarboxylate*,  $COOEt \cdot CH \langle \begin{smallmatrix} NH \\ N \cdot SO_3K \end{smallmatrix} \rangle$ . This sub-

stance forms fascicular bundles of prisms, which are very soluble in water, and melt and froth up at  $174^{\circ}$ ; if boiled with water or dilute acid for some time, it is decomposed into hydrazine and ethylic glyoxylate. When the salt is allowed to stand with dilute sulphuric acid at the ordinary temperature, the hydrazine which is formed is accompanied by the products of decomposition of ethylic glyoxalate, namely: formaldehyde, carbonic anhydride, and alcohol. *Di-*

*potassium sulphohydrazimethylenecarboxylate*,  $COOK \cdot CH \langle \begin{smallmatrix} NH \\ N \cdot SO_3K \end{smallmatrix} \rangle$ , is formed when the foregoing compound is boiled with aqueous potash.



It crystallises with  $1\text{H}_2\text{O}$  in colourless prisms, and is decomposed by acids with formation of hydrazine. A. H.

**Condensation of Aldehydes with Ketones.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, **120**, 1269—1272).—The condensation with acetone, already observed in the case of isovaleraldehyde (*Abstr.*, 1894, i, 224), is a general reaction for the saturated aldehydes of the acetic series, with the exception of formaldehyde and acetaldehyde, which act in a more energetic manner and yield different products.

Propaldehyde and acetone in presence of water and sodium hydroxide react with development of heat, and yield *propylideneacetone*,  $\text{CHEt}:\text{CH}:\text{COMe}$ , a liquid which obstinately retains water. Its oxime is a colourless, viscous liquid, which boils at  $85^\circ$  under a pressure of 6 mm.; its acetate boils at  $114^\circ$  under a pressure of 9 mm., and its sp. gr. = 1.0005 at  $0^\circ$ . *Isobutylideneacetone* boils at  $153\text{--}155^\circ$ ; its oxime is a colourless, oily liquid, which boils at  $100^\circ$  under a pressure of 6 mm., and its sp. gr. = 0.9322 at  $0^\circ$ . The acetate of the oxime is an oily liquid which has a disagreeable odour, and boils at  $126^\circ$  under a pressure of 10 mm.; sp. gr. = 0.9775 at  $0^\circ$ .

The constitution of the non-saturated ketones thus obtained by condensation indicates the possibility of the occurrence of stereoisomerism analogous to that existing between maleic and fumaric acids, but there is no evidence that the products described are mixtures. They do not react with a mixture of aniline and hydrogen cyanide or of hydrazine and hydrogen cyanide, nor with benzoylhydrazine.

Isoamylideneacetone (*loc. cit.*) condenses with amidoguanidine (compare Baeyer, *Abstr.*, 1894, i, 536), and the nitrate of the *isoamylideneacetoneamidoguanidine* thus has the constitution



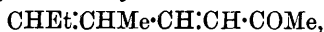
The corresponding picrate is insoluble in water, but can be crystallised from boiling alcohol.

Ænanthaldehyde and acetone, methyl propyl ketone and propaldehyde, and phenyl methyl ketone and valeraldehyde do not react in a similar manner, from which it would seem that acetone is the only ketone that condenses readily with aldehydes, and that the tendency to condense in the manner described diminishes as the molecular weight of the aldehyde increases, the condensation of the aldehyde itself eventually becoming the dominant reaction. C. H. B.

**Condensation of Valeraldehyde.** By CHARLES FRIEDEL (*Compt. rend.*, 1895, **120**, 1394).—The author has obtained the  $\alpha$ -isopropyl- $\beta$ -isobutylacraldehyde described by Barbier and Bouveault (following abstract) by the condensation of valeraldehyde in presence of sodium hydroxide. He regards it as identical with the compound of the same composition which has been obtained by several chemists in other ways, but considers that its properties are those of a ketone rather than of an aldehyde. C. H. B.

**Condensation of Unsaturated Aldehydes with Acetone.** By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895,

120, 1420—1423).—Methylethylacraldehyde when mixed with an equal weight of acetone and about 10 times its volume of water containing 0.5 per cent. of sodium hydroxide, and allowed to remain for about 24 hours, yields *methyloctadienone*.



a colourless, mobile liquid, which boils at  $97^\circ$  under a pressure of 8 mm., and has a feeble, aromatic odour; sp. gr. = 0.9170 at  $0^\circ$ . When boiled with its own weight of zinc chloride, it yields pseudo-cumene.

$\alpha$ -Isopropyl- $\beta$ -isobutylacraldehyde,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{C}(\text{CHO})\cdot\text{CHMe}_2$ , is obtained by the condensation of isovaleraldehyde under the same conditions as lead to the production of methylethylacraldehyde. It is a colourless liquid, which boils at  $73^\circ$  under a pressure of 6 mm.; its oxime is a colourless, oily liquid, boiling at  $115^\circ$  under a pressure of 8 mm.; sp. gr. = 0.9147 at  $0^\circ$ ; the nitrile is a very mobile liquid, boiling at  $88$ — $89^\circ$  under a pressure of 8 mm.; sp. gr. = 0.8637 at  $0^\circ$ .

When mixed with acetone in presence of dilute sodium hydroxide solution, it yields the compound

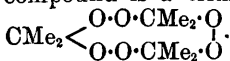


which, according to the Geneva nomenclature, is 8-methyl-5-isopropyl-3:5-nonadiene-2-one. It is a colourless, somewhat viscous liquid, which boils at  $123$ — $125^\circ$  under a pressure of 6 mm. When heated with zinc chloride, it yields metaisopropylcymene, which has an odour resembling that of cymene, and boils at about  $220^\circ$ ; sp. gr. = 0.880 at  $0^\circ$ . Some cymene is formed at the same time, most probably as a result of the partial decomposition of the isopropylcymene.

C. H. B.

### Action of Hydrogen Peroxide on Acetone and Mesityl oxide.

By RICHARD WOLFFENSTEIN (*Ber.*, 1895, 28, 2265—2269).—Hydrogen peroxide in dilute solution (1 per cent.) has no action on acetone. With a 10 per cent. solution of the peroxide, a small quantity of a crystalline substance is obtained, which melts at  $97^\circ$ , is insoluble in water, acids, and alkalis, but readily soluble in benzene, acetone, and ether; it slowly loses weight when left in the air, and more rapidly over sulphuric acid. The molecular weight, determined in benzene solution, agrees with the formula  $(\text{C}_3\text{H}_6\text{O}_2)_3$ , thus indicating that the compound is a trimolecular acetone peroxide, with the constitution



An almost theoretical yield of the substance may be obtained by mixing the acetone and hydrogen peroxide (50 per cent.) in molecular proportions, and then adding a drop of phosphoric acid. It is not acted on by acetic anhydride; on warming with dilute sulphuric acid, it is decomposed into acetone and hydrogen peroxide; and is characterised by its explosiveness.

When hydrogen peroxide (10 per cent. solution) is allowed to remain in contact with mesityl oxide for several months at the

ordinary temperature, a crystalline substance,  $(C_6H_{11}O_3)_2$ , is obtained. It is quite neutral, melts without decomposition at  $123^\circ$ , and is insoluble in dilute acids and alkalis. The constitution is given as  $OH \cdot CMe_2 \cdot CAc(OH) \cdot CAc(OH) \cdot CMe_2 \cdot OH$ . J. J. S.

**Synthesis of a Methylheptenone Methyl Butylideneethyl Ketone.** By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1895, **28**, 2115—2126).—The authors have attempted to synthesise the isoamylideneacetone which they have previously obtained by the oxidation of various members of the geraniol series, especially of geranaldehyde (citrals),  $CHMe_2 \cdot CH_2 \cdot CH : CH \cdot CMe : CH \cdot CHO$  (*Abstr.*, 1894, i, 83).

Various attempts to condense isovaleraldehyde with acetone have shown that the chief product is the diisovaleraldehyde which is obtained by the condensation of two molecules of the valeraldehyde. Small quantities of other compounds were also formed, but they could not be isolated in a pure form; the fraction  $160\text{--}180^\circ$  probably contains the isoamylideneacetone,



formed by the condensation of 1 mol. of isovaleraldehyde with 1 mol. of acetone.

The authors show that the diisovaleraldehyde prepared by Barbier and Bouveault's method (preceding page) is identical with the diisovaleraldehyde prepared by other methods (compare Friedel, this vol., i, 643, and L. Kohn, *Compt. rend.*, **121**, 259).

When the ethylic isoamylideneacetoacetate of Claisen and Matthews (*Annalen*, **218**, 174) is hydrolysed at a low temperature with a 2.5 per cent. potassium hydroxide solution and the resulting ketonic acid heated, an oil which boils at  $255\text{--}260^\circ$  is obtained instead of isoamylideneacetone. This oil is probably a polymeride of the desired ketone; but in any case the reaction indicates that isoamylideneacetone is an extremely unstable substance, and in this respect differs from the natural methylheptenone.

Under special conditions, isovaleraldehyde may be made to condense with acetylacetone to form the diketone,



which distils under atmospheric pressure at  $218\text{--}220^\circ$ . It contains a hydrogen atom which can readily be displaced by metals.

The copper derivative,  $Cu(C_{10}H_{16}O_2)_2$ , is readily prepared by shaking an ethereal solution of the ketone with an aqueous solution of copper sulphate to which insufficient alkali for the complete precipitation of the copper has been added; this copper salt is soluble in ether, and is obtained in a crystalline form when the ether is allowed to evaporate.

The calcium derivative may be obtained by treating an ethereal solution of the ketone with dry calcium hydroxide, it is more sparingly soluble in ether than the copper compound. Methyl butylideneethyl ketone,  $CHMe_2 \cdot CH : CH \cdot CH_2 \cdot COMe$ , is readily obtained when the copper derivative is mixed with an excess of calcium hydroxide in the form of a cream, and then submitted to steam distillation; it is an oily substance which boils at  $163^\circ$ , and resembles

the natural methylheptenone in most of its physical properties, but the physical constants for the two are by no means identical.

Its *oxime* distils at  $122^{\circ}$  under a pressure of 28 mm., and at  $108-110^{\circ}$  under a pressure of 15 mm.

The *semicarbazone* melts at  $115^{\circ}$  after several recrystallisations, whereas the semicarbazone prepared from the natural product melts at  $136-138^{\circ}$ . The synthetical methylheptone is also much more readily decomposed by acids and alkalis than the natural product.

As the natural methylheptenone can thus have neither of the following constitutions,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$  or



it follows that it must have the formula  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$  (see following abstract).

J. J. S.

**Natural Methylheptenone (Methyl Isopropylidenepropyl Ketone), Linaloöl, and Geraniol.** By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 2126—2137).—From synthetical experiments, it has been shown (see preceding abstract) that the natural methylheptenone, which usually accompanies geranaldehyde, linaloöl, and geraniol in various ethereal oils, and which can readily be obtained by the gentle oxidation of one of these compounds, has the constitution  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ .

The authors now show that the behaviour of the compound on oxidation supports this formula.

The ketone is oxidised in the cold with a very dilute permanganate solution, according to Wagner's method (*Abstr.*, 1890, 1313). By this means, the double bond is ruptured and two hydroxyl groups are added, thus forming a saturated glycol, which, in its turn, is oxidised by a mixture of chromic and sulphuric acids.

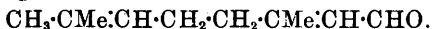
The first product of the oxidation of the natural methylheptenone is a syrup, which, when further oxidised with chromic acid, yields acetone (characterised by its parabromophenylhydrazone, m. p.  $94-95^{\circ}$ ) and levulinic acid (characterised by its phenylhydrazone). This decomposition of the ketone into levulinic acid and acetone agrees with the constitution of the ketone given above.

The two aliphatic alcohols, geraniol, and linaloöl also yield considerable quantities of acetone and of levulinic acid when oxidised in a similar manner. The authors argue that linaloöl must therefore contain the grouping  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}$ , and as it is an optically active alcohol must also contain an asymmetric carbon atom, giving the constitution  $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$ .

Geraniol, on the other hand, is an optically inactive primary alcohol, and hence has the formula  $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ .

The authors consider that the alcohols, lavendol, nerolol, aurantiol, licareol, &c., are mostly mixtures of geraniol, and dextro- or lævo-linaloöl, with small quantities of other alcohols, which give them their characteristic odours.

Geranaldehyde, which is the aldehyde corresponding with the primary alcohol geraniol, has the constitution



A mixture of several isomeric compounds is obtained when the aldehyde is treated with semicarbazide. The authors have isolated a carbazone which melts at 130—135°, whereas Wallach gives the melting points of the geranaldehyde carbazones as 150° and 160°.

Geranaldehyde is readily converted into cymene by the action of potassium hydrogen sulphate, hydriodic acid, acetic acid, &c., the condensation being preceded by a displacement of the double bonds.

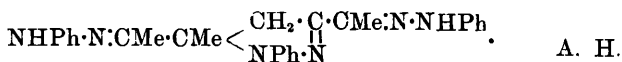
The authors criticise some of the conclusions drawn by Barbier and Bouveault (*Abstr.*, 1894, i, 401) from the oxidation of geranaldehyde and its derivatives in strongly acid solution. They point out that geranaldehyde derivatives are readily converted into terpin derivatives by the action of acids. J. J. S.

**$\alpha$ -Diketones.** By LUDWIG CLAISEN (*J. pr. Chem.*, 1895, [2], 52, 76—77).—The author agrees with Fileti and Ponzio's conclusion (this vol., i, 499) that the isonitrosoketones, prepared by Manasse and himself from the ketones  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{R}$ , have the constitution  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{NOH})\cdot\text{R}$ , and not  $\text{NOH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{R}$ , as he at first suggested. It is curious that amylic nitrite should attack the  $\text{CH}_2$  group, for ethylic acetate attacks the  $\text{CH}_3$  group, the compound  $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{R}$  being formed. C. F. B.

**The Aldol of Diacetyl.** By HANS V. PECHMANN and EDGAR WEDEKIND (*Ber.*, 1895, 28, 1845—1847).—The substance previously described as dimethylquinogen,  $\text{COMe}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COMe}$  (*Abstr.*, 1888, 811), contains 1 mol. of water more than is indicated by the above formula, and is the aldol of diacetyl,



It is a thick, odourless, colourless oil, and boils unchanged at 128° under a pressure of 18 mm. It is converted by alkalis into paraxyloquinone, but it has not yet been found possible to convert it into dimethylquinogen. The "trihydrazone" is most probably a substituted pyrazoline of the constitution



**Constitutional relations of Ricinoleic and Oleic acids.** By OTTO BEHREND (*Ber.*, 1895, 28, 2248—2250).—When the ethylic chloroketostearate of Goldsobel (this vol., i, 81) is treated with sodium amalgam, an *unsaturated acid*,  $\text{C}_{18}\text{H}_{32}\text{O}_2$ , which melts at 58°, is formed. This is either 9-keto-11:12-oleic acid or 9-keto-12:13-oleic acid. *Chloroketostearic acid* (m. p. 64°) yields the same unsaturated acid when similarly treated. When a boiling acetic acid solution of the chloroketostearic acid is treated with zinc and a little hydrochloric acid, it yields stearolic acid,  $\text{C}_{18}\text{H}_{32}\text{O}_2$ , thus losing the elements of water besides having hydrogen substituted for the chlorine. Ketostearic acid does not give stearolic acid under similar treatment.

The following formulæ agree with the above reactions.

Ketostearic acid =  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CO} \cdot [\text{CH}_2]_6 \cdot \text{COOH}$ .

Stearolic acid =  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{C} \cdot \text{C} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ .

Hydroxyketostearic acid =

$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ .

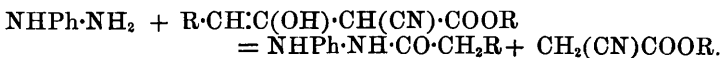
Chloroketostearic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot [\text{CH}_2]_7 \cdot \text{COOH}$ .

J. J. S.

**Methenic and Methinic acids: Ethereal Cyanacetoacetates.** By ALBIN HALLER (*Compt. rend.*, 1895, **120**, 1193—1197).—The author proposes the term *methenic acids* to denote compounds which contain the group  $\text{CH}_2\text{RR}'$ , and *methinic acids* to denote those which contain the group  $\text{CHRR}'\text{R}''$ , all the radicles in both cases being electronegative. Compounds containing the group  $\text{NHR}'\text{R}'$  might be called *imidic acids*. This classification into methenic and methinic acids is, however, based on a static view of their constitution, whereas many of the compounds which contain these groups seem to be tautomeric. Brühl and Perkin regard the compounds  $\text{CH}_2\text{Ac} \cdot \text{COOR}$  and  $\text{CO}(\text{CH}_2 \cdot \text{COOR})_2$  as ethereal ketonic derivatives whilst acetylacetone and the ethereal salts of diacetylacetic and acetylmalonic acids are regarded as unsaturated molecules in which the ketonic function is converted into an enolic function (*Abstr.*, 1894, ii, 433). According to Claisen, the introduction of new negative radicles into the groups  $\text{CH}_2$  and  $\text{CH}$ , increases the tendency to become enolic, whilst the substitution of positive radicles has the opposite effect.

When the ethereal salts of acetocyanacetic acid and its homologues (*Abstr.*, 1888, 818) are brought into contact with phenylhydrazine, they either combine with two molecular proportions of it, or yield acetylphenylhydrazine and its homologues, according to the temperature at which the action takes place. The first reaction can only be explained by assuming that the alkylic cyanacetoacetates have the constitution  $\text{R} \cdot \text{CH} \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CN}) \cdot \text{COOR}$ , analogous to that attributed by Brühl to ethylic acetylmalonate, their acid functions being due to the presence of the group  $\cdot \text{CH}(\text{CN}) \cdot \text{COOR}$  and the enolic group. The compounds with phenylhydrazine will then have the constitution  $\text{R} \cdot \text{CH} \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CN})(\text{COOR}) \cdot \text{N}_2\text{H}_4\text{Ph}, \text{N}_2\text{H}_5\text{Ph}$ .

The second reaction, which takes place when the substances are heated, is represented by the equation



The compounds with phenylhydrazine are readily obtained by direct combination in presence of ether, and considerable heat is developed by the action. They crystallise readily, but are somewhat unstable, becoming yellow when exposed to light, and are decomposed by ordinary solvents. The compound with *methylic cyanacetoacetate* crystallises in plates which melt at  $87^\circ$ ; with *ethylic cyanacetoacetate*, white plates melting at  $86^\circ$ ; with *ethylic cyanopropionylacetate*, plates which melt at  $87^\circ$ ; with *ethylic cyanobutyrylacetate*, plates which melt at  $85^\circ$ ; with *ethylic cyanisobutyrylacetate*, slender

needles melting at  $67^{\circ}$ . With *ethylic cyanisovaleroacetate* the product melts at  $65^{\circ}$ , and with the methylic salt at  $76.5^{\circ}$ .

All these compounds, when heated, yield the corresponding homologue of acetylphenylhydrazine.

*Butyrylphenylhydrazine* forms flattened needles which melt at  $104^{\circ}$ , and are soluble in boiling water and ordinary solvents. *Isobutyrylphenylhydrazine* forms white plates melting at  $143^{\circ}$ . *Isovalerylphenylhydrazine* forms transparent, rhombic tables which melt at  $112^{\circ}$ .

C. H. B.

#### Electrical Conductivity of some $\beta$ -Ketonic Ethereal Salts.

By J. GUINCHANT (*Compt. rend.*, 1895, 120, 1220—1223).—For acetylacetone, by Kohlrausch's method,  $k = 0.00015$  at  $25^{\circ}$ . Methylic and ethylic acetoacetates, methylic malonate, and methylic cyanacetate, malononitrile, methylic acetylmalonate, and ethylic diacetoacetate show conductivities which are somewhat feeble, but tend to increase with time, especially in the case of the last two compounds, probably owing to interaction with water. It is especially noteworthy that the only compounds which show any decided conductivity are those which are regarded by Brühl and by Perkin as containing the group C.OH, which is found in the carboxylic acids, phenols, normal cyanic acid,  $\alpha$ -hydroxyquinoline, &c. Ethylic acetoacetate and ethylic malonate, which contain the ketonic group, are practically non-conductors.

The sodium salts of the cyanomethenic acids (preceding abstract), on the other hand, show a normal conductivity, and, like acetylacetone, obey Ostwald's law ( $k = \text{const.}$ ) as closely as could be expected, having regard to the fact that the compounds have both an acidic and an ethereal function. In those cases where the heats of neutralisation have been determined, the chemical activity deduced from the thermochemical results agrees with that deduced from the conductivity.

As a rule, in series of homologous acids, the value of  $k$ , and consequently the chemical activity, diminishes as the atomic weight increases.

C. H. B.

#### Preparation and Conductivity of Alkylcy Cyanomethinates.

By J. GUINCHANT (*Compt. rend.*, 1895, 121, 71—73; compare preceding abstract).—The compounds described were prepared by Haller's method of acting on an alkylcy sodiocyanacetate with an acid chloride. *Methylic cyanopropionylacetate* forms crystals which melt at  $39$ — $40^{\circ}$ ; it boils at  $130^{\circ}$  under a pressure of 43 mm. *Methylic cyanobutyrylacetate* crystallises in needles melting at  $0^{\circ}$ , and boils at  $135.5^{\circ}$  under a pressure of 25 mm.; the *isobutyryl* compound forms octahedral crystals melting at  $36$ — $37^{\circ}$ , and boils at  $139^{\circ}$  under a pressure of 48 mm. *Propylic cyanacetoacetate* melts at  $35$ — $36^{\circ}$  and boils at  $133^{\circ}$  under a pressure of 25 mm.; the *isobutylic* salt does not crystallise at  $-15^{\circ}$ , and boils at  $142^{\circ}$  under a pressure of 32 mm.; the *amylic* salt does not crystallise at  $-15^{\circ}$ , and boils at  $168^{\circ}$  under a pressure of 46 mm. All these compounds give a red coloration with ferric chloride solution, and form insoluble cupric salts; they displace acetic acid from its zinc and silver salts and form

white precipitates insoluble in acetic acid. The sodium salts crystallise as hydrates; the anhydrous salts are more deliquescent the higher their atomic weights.

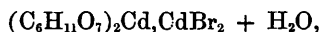
The conductivity of solutions of these ethereal salts indicates that they are monobasic acids. The difference  $\mu_{1024} - \mu_{32}$  varies from 10 to 12; the value of  $\mu_{\infty}$  is 351—352, and the value of  $k$  varies between 0.50 and 0.73.

The conductivity decreases slowly with time, probably in consequence of the decomposition of the ethereal salt by water. The conductivity of the alkylic cyanomethenates diminishes as the molecular weight increases in the first three terms, but rises in the case of isobutylic cyanacetoacetate. Ostwald observed a similar change at the fourth term in the acids of the acetic series. C. H. B.

**Idonic acid, Idose, Iditol, and Idosaccharic acid.** By EMIL FISCHER and IRVING WETHERBEE FAY (*Ber.*, 1895, **28**, 1975—1983).—These names are used to denote the last remaining members of the group of substances isomeric with mannitol and its derivatives, *l*-idose

being itself  $\text{OH} \cdot \text{CH}_2 \cdot \overset{\text{H}}{\underset{\text{OH}}{\text{C}}} - \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} - \overset{\text{H}}{\underset{\text{OH}}{\text{C}}} - \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} \cdot \text{CHO}$ . *l*-Idonic acid is prepared

from xylose by means of hydrocyanic acid, in the same way as *l*-gulonic acid (*Abstr.*, 1891, 667), the mixture being allowed to remain 6—10, instead of 2, days. A mixture of *l*-idonic and *l*-gulonic acids is obtained, and these are separated by means of their brucine salts, which are soluble in 200 and 50 parts respectively of methylic alcohol, and melt and decompose at 180—185° (corr. 185—190°) and 155—158°. These two acids can be converted each into the other by heating with pyridine and water at 140°. The salt,



is characteristic of *l*-idonic acid; the specific rotation is  $[\alpha]_{\text{D}} = -3.25$  at 20°. By reducing a syrupy mixture of this acid and its lactone, with 2½ per cent. sodium amalgam, *l*-idose is obtained as a syrup which reduces Fehling's solution, but does not undergo fermentation with yeast; its osazone is indistinguishable from gulosazone. By further reduction, it yields *l*-iditol, which was obtained as a syrup; a derivative of this, *tribenzylideneiditol*,  $\text{C}_6\text{H}_5\text{O}_6(\text{CHPh})_3$ , softens at 215°, and melts at 219—223° (corr. 224—228°), and dissolves in 105 parts of acetone; *tribenzylidenemannitol* melts at 213—217° (corr. 218—222°), and dissolves in 34.5 parts of acetone. *l*-Idosaccharic acid is obtained by the oxidation of *l*-idonic acid with nitric acid at 50°; it is a syrup, and forms a *copper salt*,  $\text{C}_6\text{H}_5\text{O}_6\text{Cu} + 2\text{H}_2\text{O}$ ; the specific rotation is greater than  $-100^\circ$ . This acid replaces the once accepted isosaccharic acid in the group of compounds alluded to above.

Optical antipodes of all the above substances can be prepared, starting from *d*-idonic acid, which is obtained by heating *d*-gulonic acid (itself prepared from saccharolactone) with pyridine and water at 140°. These *d*-compounds resemble the *l*-modifications entirely,



yielding salts with identical composition and melting points, and having a rotation of the same amount but of opposite sign (+).

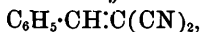
C. F. B.

**Condensation of Aromatic Aldehydes with Cyanacetamide, Malonamide, and Malononitrile.** By R. HEUCK (*Ber.*, 1895, 28, 2251—2256; compare Ogialoro, *Abstr.*, 1879, 640; V. Meyer, *Ber.*, 21, 355; Carrick, *Abstr.*, 1892, 1086; Fiquet, *Abstr.*, 1892, 1340; and Bechert, *Abstr.*, 1894, i, 488).—The author shows that cyanacetamide yields condensation products with benzaldehyde and with furfuraldehyde according to the scheme  $R \cdot CHO + CH_2(CN) \cdot CONH_2 = R \cdot CH:C(CN) \cdot CONH_2 + H_2O$ ; and that malonamide and malononitrile react in a similar manner.

$\alpha$ -Cyan- $\beta$ -furfurylacrylamide,  $C_4OH_3 \cdot CH:C(CN) \cdot CONH_2$ , is readily obtained when a mixture of furfuraldehyde is heated with cyanacetamide in molecular proportion, first alone, and then with a small quantity of sodium ethoxide. It crystallises in yellow, glistening needles, melts at  $156^\circ$ , and is only sparingly soluble in cold water, benzene, or chloroform. When treated with phosphorus pentachloride, it yields *furfurylidenemalononitrile*,  $C_4OH_3 \cdot CH:C(CN)_2$ , which may also be obtained by the action of furfuraldehyde on malononitrile. It melts at  $76^\circ$  and gives a blue coloration with alcoholic potash. The chloride of cyanofurfurylacrylic acid, obtained by the action of phosphorus pentachloride on the acid, melts at  $79^\circ$ , and is readily soluble in ether, chloroform, benzene and hot light petroleum. When warmed with water, it is rapidly converted into the acid, with alcohol, it gives the ethylic salt, and with dry ammonia, the amide (see above). The amide, when boiled with a mixture of sulphuric acid (1 part) and water (3 parts), yields the acid; whereas, when boiled with aqueous potash, it gives a substance which is isomeric with the amide; this melts at  $150^\circ$ , is readily soluble in alkalis, and is reconverted into the amide when heated at  $160^\circ$ .

*Furfurylidenemalonamide*,  $C_4OH_3 \cdot CH:C(CONH_2)_2$ , which melts at  $200^\circ$ , is only sparingly soluble in alcohol or in water, but readily in acetic acid.

$\alpha$ -Cyanocinnamamide,  $C_6H_5 \cdot CH:C(CN) \cdot CONH_2$ , melts at  $123^\circ$ , and is readily soluble in chloroform and alcohol. When treated with phosphorus pentachloride, it yields *benzylidenemalononitrile*,



which may also be obtained by heating benzaldehyde and malononitrile with a small quantity of sodium ethoxide. It crystallises in glistening needles which melt at  $87^\circ$ .

*Benzylidenemalonamide*,  $C_6H_5 \cdot CH:C(CONH_2)_2$ , melts at  $189$ — $190^\circ$ , and, when treated with phosphorus pentachloride, yields the corresponding nitrile.

J. J. S.

**Nitrofurfuryl Derivatives.** By R. HEUCK (*Ber.*, 1895, 28, 2256—2258; compare Priebs, *Abstr.*, 1885, 971).—*Ethylic nitrofurfuryl cyanacrylate*,  $NO_2 \cdot C_4OH_2 \cdot CH:C(CN) \cdot COOEt$ , obtained by adding ethylic furfurylcyanacrylate to well cooled concentrated nitric acid, crystallises in yellow plates, melts at  $153^\circ$ , and is readily soluble in alcohol, benzene, chloroform, and acetic acid.

*Nitrofurfurylecyanacrylic acid* forms yellow crystals and decomposes at 250°. It is readily decomposed by aqueous or alcoholic alkali, but yields an ammonium salt when ammonia is passed into a cooled solution of the acid in absolute alcohol. The *silver salt* forms a yellow precipitate.

*Nitrofurfurylidenemalononitrile*,  $\text{NO}_2 \cdot \text{C}_4\text{OH}_2 \cdot \text{CH}:\text{C}(\text{CN})_2$ , crystallises in yellow, glistening, rhombic plates, and melts at 179°.

*Ethylic nitrofurfurylidenemalonate* melts at 108°. The author has not succeeded in reducing these compounds to the corresponding amido-derivatives. J. J. S.

**Hexachlorobenzene Paradichloride.** By ÉTIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], 13, 418—423).—By the action of phosphorus pentachloride on  $\alpha$ -hexachlorophenol or tetrachloroquinone, an octochloro-derivative of benzene is formed, whose constitution has an important bearing on that of quinone (compare this vol., i, 655).

The hexachlorophenol (300 grams) is heated with phosphorus pentachloride (215 grams) for 48 hours at 130—135°, or the tetrachloroquinone (32 grams) with the chloride (52 grams) for three days at the same temperature, or, in presence of phosphorus trichloride, for half that time. The product, which solidifies on cooling, is washed with alkali and water and crystallised from benzene, the mixture of needles of hexachlorobenzene and prisms of the dichloride thus obtained being separated by hand.

*Hexachlorobenzene paradichloride*,  $\text{C}_6\text{Cl}_8$ , forms large, colourless, triclinic prisms or plates, sp. gr. = 2.0618 at 18°, and melts, and to some extent sublimes, at 159—160°. It is insoluble in water, but dissolves in the usual organic solvents. By the action of heat (204°) on the pure substance, or that of chlorine on its carbon tetrachloride solution in presence of antimonious chloride, it is resolved into hexachlorobenzene and chlorine. It is not affected by chlorine in presence of sunlight or of iodine, but is reduced by sodium amalgam to hexachlorobenzene and hydrogen chloride, and is decomposed in a similar manner by prolonged boiling with alcoholic potash, although it is stable towards aqueous potash. Hexachlorobenzene paradichloride is oxidised, completely by nitric acid, and partially by sulphuric acid, to tetrachloroquinone.

The ease with which this octochlorobenzene is formed from, and converted into tetrachloroquinone, leaves no doubt that its constitution is  $\text{CCl}_2 < \begin{smallmatrix} \text{CCl}:\text{CCl} \\ \text{CCl}:\text{CCl} \end{smallmatrix} > \text{CCl}_2$ .

*Pentachlorophenyl dihydrogen phosphate*,  $\text{CCl}_5\text{O} \cdot \text{PO}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , occurs as a bye-product in both methods of preparation. It forms colourless, transparent crystals, and melts at 224°. JN. W.

**Compounds of Symmetrical Trinitrobenzene.** By PIETER VAN ROMBURGH (*Rec. Trav. Chim.*, 1895, 14, 65—70).—Trinitrobenzene is readily separated from its unsymmetrical isomeride by means of its additive compound with dimethylaniline; the base is added to the alcoholic solution of the mixture, and the insoluble additive compound decomposed with dilute hydrochloric acid.

Symmetrical trinitrobenzene forms additive compounds with various nitrogen bases when mixed with them in alcoholic solution. The *brucine* compound,  $C_6H_3(NO_2)_3 \cdot C_{23}H_{26}N_2O_4$ , forms slender, brownish-red needles, having a brilliant lustre, and melts and decomposes at  $158^\circ$ , but no compounds could be obtained with strychnine, morphine, quinine, quinidine, or hydrastine, although colour changes were observed on mixing solutions of trinitrobenzene with daturine, carpine, and codeine. The *indole* compound,  $C_6H_3(NO_2)_3 \cdot C_8H_7N$ , forms golden-yellow needles, and melts at  $187^\circ$ ; it is stable towards hydrochloric acid, but is partially decomposed into its proximate constituents by benzidine. The *scatole* compound appears to be of the same type; it forms slender, red needles, and melts at  $183^\circ$ . The *pyrroline* compound,  $C_6H_3(NO_2)_3 \cdot C_4NH_5$ , forms long, very brilliant, yellow needles, and melts at  $95^\circ$ , at the same time decomposing into its proximate constituents; it is very unstable, and readily loses pyrroline when dissolved in alcohol, or exposed to the air.

No compounds could be formed with pyridine or quinoline, but a dark red, resinous product is formed when piperidine is heated with trinitrobenzene in alcoholic solution; the piperidine possibly acts as a reducing agent, as a similar action seems to take place with phenylhydrazine.

The *nitrodimethylmetaphenylenediamine* compound,



forms slender brick-red or crimson needles, and melts at  $130^\circ$ , after softening at  $125^\circ$ . The *nitrotrimethylmetaphenylenediamine* compound forms small red needles, and melts at  $144^\circ$ . JN. W.

**Action of Sodium and Caustic Alkalis on Polynitro-derivatives.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, 14, 89—94).—The peculiar colour changes brought about by the action of alkalis on di- and tri-nitrobenzoic acids can hardly be due, as V. Meyer supposes, to the formation of metallic substitution products, for sodium has no action on trinitrobenzene, although this substance also yields a coloration when digested with alkali. The nuclear hydrogen of the di- and tri-nitrobenzenes and their homologues is, in fact, not displaceable by sodium, even when the hydrogen is in the most favourable position, between two meta-nitro-groups; any of the dinitrobenzenes, or symmetrical trinitrobenzene, or its toluene or xylene homologues, may be boiled with sodium in benzene or toluene solution for hours without undergoing any appreciable change.

The *colouring matter* formed by the action of alkalis on trinitrobenzene may be obtained in red crystals, having a green, metallic lustre, by adding cold, concentrated, aqueous potash to a methylic alcohol solution of the nitro-compound. It is probably an additive compound, but is still under investigation. It is slowly decomposed by water into tetranitroazoxybenzene and potassium nitrite. The action of potash on trinitrobenzene is thus remarkably different from that of soda, by which the nitro-compound is decomposed into sodium nitrite and dinitroanisole. JN. W.

**Influence of the Methyl group on the Properties of Nitro-groups.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 95—97).—The action of caustic soda on symmetrical trinitrotoluene and trinitro-xylene is much more complex than that on trinitrobenzene, as instead of dinitroanisols, brown, amorphous products are formed, soluble in water, and reprecipitated by acids and metallic salts. They are probably azoxy-compounds, formed by reduction of the nitro-compounds.

A similar product is formed by the action of alcoholic potassium cyanide on metadinitrobenzene, and is perhaps due to a similar cause, the entrance of the cyanogen radicle into the 1 : 2 : 3-ethoxycyanonitrobenzene which is formed, resulting from the oxidation of the metal of the cyanide and the hydrogen of the nucleus by other molecules of the dinitro-compound. In the case of dinitrotoluene, the amorphous reduction product is alone formed.

The introduction of a methyl group or groups into the nitrated ring has thus the effect in both cases of favouring the more complex reaction.  
JN. W.

**5-Chlorodihydrometaxylene.** By A. KLAGES and EMIL KNOEVENAGEL (*Ber.*, 1895, **28**, 2044—2048; compare this vol., i, 86).—The action of cold dilute nitric acid converts chlorodihydrometaxylene into dimethyl- $\Delta_2$ -ketotetrahydrobenzene; if, however, 30 per cent. nitric acid is employed and heated with the substance for 24 hours in a reflux apparatus, nitrochlorometaxylene and symmetrical chlorotoluic acid are formed, a polynitro-derivative and chloropicrin being produced at the same time.

*Nitrochlorometaxylene* [ $\text{Me}_2 : \text{NO}_2 : \text{Cl} = 1 : 3 : 4 : 5$ , or  $1 : 3 : 2 : 5$ ], forms colourless crystals, and melts at  $48-49^\circ$ ; it dissolves readily in organic solvents, is volatile in an atmosphere of steam, and distills without decomposing.

*Symmetrical chlorotoluic acid* crystallises from dilute alcohol, and melts at  $178^\circ$ ; oxidation of the feebly alkaline solution with potassium permanganate converts it into symmetrical chlorisophthalic acid and hydroxysophthalic acid.

When chlorodihydrometaxylene is slowly dissolved in ice-cold fuming nitric acid, and then allowed to remain at the ordinary temperature, a vigorous action takes place; equal parts of fuming nitric acid and 15 per cent. fuming sulphuric acid are then added to the liquid, which is boiled in a reflux apparatus for half an hour. On cooling the acid liquid, *symmetrical trinitrochlorometaxylene* separates in lustrous, white leaflets; it crystallises from alcohol in white needles, and melts at  $218^\circ$ . When heated with alcoholic ammonia at  $130^\circ$ , it yields *symmetrical trinitrometaxylidine*, which melts at  $206^\circ$ ; this base sublimes when carefully heated, and crystallises from dilute alcohol in yellowish-brown needles. *Symmetrical trinitrophenylamidometaxylene* is obtained by heating trinitrochlorometaxylene with aniline at  $150^\circ$ ; it crystallises from alcohol in long, lustrous, yellow needles, and melts at  $175^\circ$ .

Chlorodihydrometaxylene is readily attacked by a cold solution of potassium permanganate, a small quantity of symmetrical chloro-

xylene being formed. This result is also effected by potassium dichromate or a solution of chromic anhydride in glacial acetic acid.

M. O. F.

**Trimethylethylbenzene.** By PAUL JANNASCH and J. H. WIGNER (*Ber.*, 1895, **28**, 2027—2028).—2 : 4 : 6-Trimethylethylbenzene,  $C_6H_2Me_3Et$ , is best prepared by heating a mixture of 25 grams of bromomesitylene, 32 grams of ethylic iodide, 14 grams of sodium in thin shavings, and 25 c.c. of xylene at  $180^\circ$  in a paraffin bath. The reaction also takes place in ethereal solution at the ordinary temperature, but the yield is then very small. Ethyltrimethylbenzene is a faint aromatic-smelling liquid boiling at  $212$ — $214^\circ$ ; it yields crystalline bromo- nitro- and sulpho-derivatives, which are being further examined.

H. G. C.

**Constitution of  $\alpha$ -Hexachlorophenol and of Quinone.** By ÉTIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], **13**, 423—427).— $\alpha$ -Hexachlorophenol may be regarded either as a substituted ketone of the constitution  $CO \begin{smallmatrix} CCl:CCl \\ CCl:CCl \end{smallmatrix} CCl_2$  or as a pentachlorophenol hypochlorite of the constitution  $C_6Cl_5 \cdot OCl$ ; but the former view is most in accord with facts. Hexachlorophenol is converted by phosphorus pentachloride into an octochlorobenzene (this vol., i, 652) and not into a hexachlorobenzene. A second hexachlorophenol is known, melting at  $46^\circ$ , which can only be accounted for as a position isomeride,  $CCl \begin{smallmatrix} CCl:CCl \\ CO:CCl_2 \end{smallmatrix} CCl$ . Moreover, a hypochlorite would not be stable towards potash, and would not yield tetrachloroquinone on oxidation, as does  $\alpha$ -hexachlorophenol. It is true that the hexachlorophenol does not form a bisulphite compound, but this may be explained by the lack of a common solvent for the chlorophenol and the sulphite. Similarly, the absence of a phenylhydrazone may be explained by the fact that the chlorophenol does not contain hydrogen, and acts rather as a chlorinating agent towards the hydrazine. The conversion of  $\alpha$ -hexachlorophenol into perchlorodioxydiphenylene and pentachlorophenol is explained equally well by either formula.

Since  $\alpha$ -hexachlorophenol has the constitution  $CO \begin{smallmatrix} CCl:CCl \\ CCl:CCl \end{smallmatrix} CCl_2$  and its dichloro-derivative the constitution  $CCl_2 \begin{smallmatrix} CCl:CCl \\ CCl:CCl \end{smallmatrix} CCl_2$ , the constitution of quinone can only be represented by Fittig's ketonic formula,  $CO \begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix} CO$ . The only serious argument against this formula, and in favour of Graebe's para-bond formula, was the formation of hexachlorobenzene instead of an octochlorobenzene by the action of phosphorus pentachloride on quinone, and this has now been shown to be due to the decomposition of the octochloro-compound owing to the use of an unnecessarily high temperature. JN. W.

**Action of Zinc Chloride on Resorcinol.** By EDOUARD GRIMAUZ (*Compt. rend.*, 1895, **121**, 88—100).—When resorcinol is heated for five or six hours at  $135$ — $145^\circ$  with its own weight of zinc chloride,

about half of it is converted into resinous products mixed with small quantities of umbelliferone (hydroxycoumarin) melting at  $255^{\circ}$ , and another compound melting at  $261^{\circ}$ . The umbelliferone can be isolated by extracting the product with successive small quantities of boiling water, and the other product is obtained by treating the insoluble residue with boiling toluene.

The compound which melts at  $261^{\circ}$  forms small colourless needles, insoluble in water but soluble in most organic solvents. It is only slightly soluble in ammonia, but dissolves in potassium hydroxide solution, yielding a non-fluorescent liquid in both cases; it gives no coloration with ferric chloride; is decomposed when heated with zinc chloride or sulphuric acid, and the products show a green fluorescence when dissolved in solutions of alkalis; it yields no fluorescein with phthalic anhydride. It has the composition  $C_{24}H_{16}O_5$ , and seems to be formed from 4 mols. of resorcinol with elimination of  $3H_2O$ , but it is probable that part of the hydrogen eliminated is derived from the benzene nucleus.

The resinous product insoluble in water and toluene dissolves in alkalis, and yields brown-red solutions with an intense green fluorescence. It seems to be identical with the product obtained by Barth and Weidel by the action of hydrochloric acid on resorcinol at  $180^{\circ}$ , and erroneously described by them as resorcin ether. C. H. B.

**Derivatives of Eugenol.** By CARL HELL (*Ber.*, 1895, 28, 2082—2087).—Dibromoeugenol has the same phenolic character as eugenol itself, and readily yields derivatives, whilst dibromoeugenol dibromide cannot be converted into salts, ethers, &c.

Dibromoeugenol methyl ether, which was first described by Boyen (*Ber.*, 21, 1393), crystallises in white plates melting at  $29.5^{\circ}$ . It readily combines with bromine, forming *dibromoeugenol methyl ether dibromide*, which crystallises in white, silvery plates melting at  $65^{\circ}$ . *Bromoeugenol methyl ether dibromide*,  $C_6H_2Br(OMe)_2 \cdot C_3H_5Br_2$ , is formed by the action of bromine on eugenol methyl ether, although a monobromo-compound cannot be prepared from eugenol itself. It crystallises in lustrous, white needles melting at  $77^{\circ}$ . It is converted by zinc dust into *bromoeugenol methyl ether*, which is a colourless oil boiling at  $185^{\circ}$  at 40 mm. pressure. It was found impossible to prepare a dibromo-derivative directly from eugenol methyl ether. *Tribromoeugenol dibromide* is formed when the dibromo-compound is heated with bromine at  $100^{\circ}$ , but has not been obtained in the pure state. The *acetate* crystallises in short needles or plates and melts at  $137^{\circ}$ . *Tribromoeugenol acetate* is also a crystalline substance. *Dibromoeugenol ethyl ether* is a light yellow oil, which solidifies in the cold to crystals melting at  $20^{\circ}$ .

The *acetate*, prepared from dibromomethyl eugenol ether dibromide, is converted by oxidation with chromic acid into *dibromoveratric aldehyde*. The brominated ethers of eugenol are converted by alkaline permanganate into brominated veratric acids, which have been made the subject of investigation. *Dibromodimethylprotocatechuic acid* crystallises in plates and melts at  $181^{\circ}$ ; *dibromomethylethylprotocatechuic acid*

melts at 171—172°. These acids will be more fully described in a future publication. A. H.

**Derivatives of Isoeugenol.** By CARL HELL and B. PORTMANN (*Ber.*, 1895, **28**, 2088—2093).—Isoeugenol is converted by bromine into *bromisoeugenol dibromide*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Br}(\text{OH})\cdot\text{C}_3\text{H}_5\text{Br}_2$ , which melts at 138—139°. If only 1 mol. of bromine be added very carefully to an ethereal solution of isoeugenol, it is possible to obtain *isoeugenol dibromide*, which melts at about 86—87° but is exceedingly unstable. Isoeugenol therefore, in its behaviour towards bromine, differs completely from eugenol, which is at once converted into dibromeugenol dibromide. Isoeugenol methyl ether also readily combines with bromine to form the dibromide, which has been described by Ciamician and Silber (*Abstr.*, 1890, 966). The *dibromide of the ethyl ether* melts at 101—104°. The dibromides of the derivatives of isoeugenol are not attacked in alcoholic solution by zinc dust, whilst those of eugenol and its derivatives readily lose their bromine when treated in this way. The dibromide of isoeugenol ethyl ether readily reacts with sodium ethoxide to form a yellowish oil which boils at 177.5° (pressure = 16 mm.), and has the sp. gr. 1.039 at 20°. This substance has the formula  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}:\text{CMe}\cdot\text{OEt}$ , and when exposed to the air or treated with dilute acids is converted into a compound of the formula  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}:\text{CMe}\cdot\text{OH}$ , which crystallises in large tablets and melts at 56—57°. Methylisoeugenol dibromide, when treated in the same manner, yields an oil which boils at 192—193° (pressure = 15 mm.), and is converted by dilute acids into large crystals melting at 58—59°. This solid compound has the composition  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}:\text{CMe}\cdot\text{OH}$ .

Similar results have been obtained with the dibromides of anethoöl and monobromanethoöl, and will be subsequently described.

A. H.

**Preparation of the three Nitranilines.** By E. BRUNS (*Ber.*, 1895, **28**, 1954—1955).—Aniline is dissolved in 6—8 times its weight of concentrated sulphuric acid, and the solution is kept cooled and stirred in an iron or nickel crucible while it is nitrated with the calculated quantity of nitric acid mixed with an equal volume of sulphuric acid; the temperature should not rise above 0°. The mixture is then poured on to ice and diluted with ice-cold water so long as 2-nitraniline is precipitated; this is purified by one crystallisation from alcohol. The filtrate is neutralised with powdered sodium carbonate; if any resin separates at first, it is filtered off; yellowish-brown 4-nitraniline is first precipitated, and then the 3-compound, which is pure yellow in colour. The colour change is so distinct that there is no difficulty in precipitating first the one compound, and then the other, after filtering off the first; the precipitates are purified by one recrystallisation. In this way, aniline yields 10—15 per cent. of its weight of 2-nitraniline, and from 45—50 per cent. of each of the two isomerides. C. F. B.

**Aldoxime Salts.** By HEINRICH GOLDSCHMIDT and LUDWIG RÖDER (*Ber.*, 1895, **28**, 2013—2020).—The authors have examined the

lowering of the freezing point of solutions of the sodium salts of the following stereoisomeric aldoximes: syn- and anti-benzaldoxime, syn- and anti-paranisaldoxime, and syn- and anti-metanitrobenzaldoxime, and, from the results obtained, it appears that, in aqueous solutions, the anti-salts undergo almost entirely electrolytic dissociation, whilst the syn-salts, in addition to the electrolytical dissociation, also show a considerable amount of hydrolytic dissociation.

A further series of observations was made as to the alteration of the freezing point caused by the salts in strongly alkaline solutions, the syn-salts employed being those of benzaldoxime, paranisaldoxime, metanitrobenzaldoxime, and propaldoxime, and the anti-salts those of para- and orthanisaldoxime, cuminaldoxime, and metanitrobenzaldoxime. The anti-derivatives all behave in the same manner, the first addition causing a depression of the freezing point, but on further addition of the salt the freezing point rises and finally usually becomes higher than that of the original solution. Of the syn-aldoximes, the metanitrobenzaldoxime behaves in a similar manner, but the others lower the freezing point in proportion to the amount of salt added. This behaviour of the syn-salts must be due to their hydrolytic dissociation, again showing that the syn-aldoximes are much weaker acids than the anti-aldoximes. H. G. C.

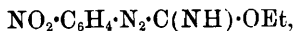
**Derivatives of the Benzenediazocarboxylic acids.** By ARTHUR HANTZSCH and O. W. SCHULTZE (*Ber.*, 1895, **28**, 2073—2082).—The derivatives of the benzenediazocarboxylic acids are obtained from the diazocyanides. The two stereoisomeric diazocyanides yield identical products, which appear to belong to the anti-series.

*Paranitrobenzenediazocarbamide*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2$ , is formed when nitrobenzenediazocyanide is boiled with water, and crystallises in long, ruby-red needles which melt at  $183^\circ$ ; it may be recrystallised from hot water, but is only sparingly soluble in cold water. *Parachlorobenzenediazocarbamide* is moderately soluble in cold water and crystallises in long, orange-coloured needles melting at  $182^\circ$ . These amides can also be prepared by dissolving the diazocyanides in concentrated sulphuric acid, and by boiling the compounds of the diazocyanides with hydrocyanic acid, as well as the diazobenzene-carboxylic imido-ethers, with water. They are converted by alcoholic potash into the salts of the corresponding acids.

*Potassium parachlorobenzenediazocarboxylate*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{COOK}$ , forms lustrous, golden-yellow plates. It may be preserved in the dry state, but decomposes when moist and when its aqueous solution is heated. The salt deflagrates when heated or when placed in sulphuric acid. The free acid is obtained as a yellow precipitate when a solution of the salt is acidified with a mineral acid; it decomposes very rapidly, chlorobenzene being among the products formed. *Potassium paranitrobenzenediazocarboxylate* crystallises in brown needles. The free acid is slightly more stable than the chlorinated acid, but could not be analysed.

The diazocyanides dissolve in alcohol with formation of the corresponding imido-ether of a benzenediazocarboxylic acid. The *ethyl-imido-ether of nitrobenzenediazocarboxylic acid*,





crystallises in orange-red needles melting at  $73^\circ$ . The corresponding *methylimido-ether* melts at  $128-129^\circ$ . These compounds do not produce any colouring matter with  $\beta$ -naphthol or R-salt. The *methylimido-ether of chlorobenzenediazocarboxylic acid* forms yellowish-brown needles melting at  $69^\circ$ . Anti-nitrodiazobenzene cyanide reacts in a remarkable manner with  $\beta$ -naphthol, a yellowish-brown reduction product of the cyanide, which has the formula  $\text{C}_7\text{H}_5\text{N}_4\text{O}_2$ , being formed along with a compound of the formula  $\text{C}_{10}\text{H}_7\text{NO}_2$ .

*Chlorodiazobenzenetolylguanidine*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , is formed by the direct union of chlorodiazobenzene cyanide with paratoluidine in alcoholic solution in presence of a few drops of aqueous soda. It forms reddish-brown crystals melting at  $167^\circ$ . The *hydrochloride* is a coloured, crystalline substance. The diazocyanides also unite with hydrogen chloride to form imidochlorides, which are exceedingly unstable.

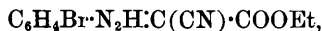
*Chlorobenzenehydrazocarbamide*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , is obtained by the reduction of chlorobenzenediazocarbamide with alcoholic ammonium sulphide. It forms white crystals, melts at  $232^\circ$ , and reduces ammoniacal silver oxide. *Chlorobenzenehydrazothiocarbamide*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$ , is obtained by passing hydrogen sulphide into an alcoholic solution of chlorobenzenediazocyanide and melts at  $198^\circ$ .

The compound of diazobenzene cyanide with hydrogen cyanide is converted by reduction into the imidocyanide of benzenehydrazo-carboxylic acid, which is identical with Fischer's dicyanophenyl hydrazine. A. H.

### Action of Diazo-compounds on Ethylic Cyanacetate.

By B. MARQUARDT (*J. pr. Chem.*, 1895, [2], 52, 160—176; compare Abstr., 1894, i, 369).—The salts previously described as labile forms of azocyanacetates (Abstr., 1894, i, 369) are probably correctly so described, whilst the stable forms are hydrazonecyanacetates. The former can be converted into the latter by heating them above their melting points, or by heating them with alcohol.

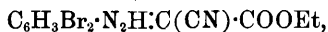
*Ethylic metabromophenylhydrazonocyanacetate*,



is prepared by diazotising a solution of bromaniline in glacial acetic acid, adding ethylic cyanacetate, cooling in a freezing mixture, and adding crystalline sodium acetate. It forms yellow crystals, melts at  $102^\circ$ , and dissolves freely in alcohol and ether, but only sparingly in benzene, chloroform, and light petroleum. By dissolving it in alcoholic potash and adding hydrochloric acid to the solution, *ethylic azobromobenzenecyanacetate*,  $\text{N}_2\text{Ph} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$ , is precipitated; this melts at  $153^\circ$ , and is converted into the phenylhydrazonocyanacetate when heated with alcohol. The isomerides differ from each other in their solubility in benzene, the stable form (m. p.  $102^\circ$ ) being six times as soluble as the labile form. When ethylic metabromophenylhydrazonocyanacetate is heated with aqueous potash, it yields

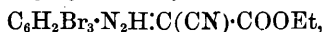
*bromophenylhydrazonacetic acid*, which melts at  $167^{\circ}$  and gives precipitates with solutions of most metallic salts.

*Ethylic dibromophenylhydrazoncyanacetate*,



is prepared in a similar manner from dibromaniline [ $\text{NH}_2 : \text{Br}_2 = 1 : 2 : 5$ ], but the yellow crystals obtained in this way melt at  $160^{\circ}$ , and appear to be a mixture of the two isomerides, for when they are dissolved in potash, hydrochloric acid precipitates the labile form (*ethylic azodibromobenzenecyanacetate*), which melts at  $172^{\circ}$ , whilst carbonic anhydride precipitates the stable form (the hydrazoncyanacetate), which melts at  $144^{\circ}$ . One hundred parts of benzene dissolve 0.6943 part of the labile form and 0.1159 part of the stable form.

*Ethylic tribromophenylhydrazoncyanacetate*,



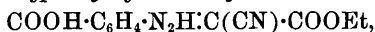
when prepared from tribromaniline ( $\text{NH}_2 : \text{Br}_3 = 1 : 2 : 4 : 6$ ) by the process described for the monobromo-derivative, crystallises in lustrous, golden laminae, which melt at  $144^{\circ}$  and therefore contain a little of the labile isomeride. When these crystals are dissolved in potash, carbonic anhydride precipitates the hydrazoncyanacetate from the solution in crystals, which melt at  $141^{\circ}$  and dissolve to the extent of 5.103 parts in 100 parts of benzene at  $15^{\circ}$ . The labile form (*ethylic azotribromobenzenecyanacetate*) is precipitated from the potash solution by hydrochloric acid; it melts at  $134^{\circ}$ , and dissolves to the extent of 8.852 parts in 100 parts of benzene.

*Ethylic  $\alpha$ -naphthylhydrazoncyanacetate*,  $\text{C}_{10}\text{H}_7\cdot\text{N}_2\text{H}\cdot\text{C}(\text{CN})\cdot\text{COOEt}$ , is prepared from  $\alpha$ -naphthylamine by diazotisation and addition of ethylic cyanacetate; it forms yellow-brown crystals, melts at  $147^{\circ}$ , and dissolves to the extent of 2.3482 parts in 100 parts of benzene. When hydrolysed with alcoholic potash, it yields the corresponding acid, which forms dark yellow-brown crystals and melts at  $125^{\circ}$ . *Ethylic azo- $\alpha$ -naphthalenecyanacetate*, prepared by precipitating the potash solution of the hydrazoncyanacetate with hydrochloric acid, forms brown-red crystals, melts at  $105^{\circ}$ , and dissolves to the extent of 3.5006 parts in 100 parts of benzene.

*Ethylic  $\beta$ -naphthylhydrazoncyanacetate*, as first prepared, melts at  $142^{\circ}$ , but when separated from the labile form by dissolution in potash and precipitation with carbonic anhydride, it melts at  $145^{\circ}$  and dissolves in benzene to the extent of 2.571 parts in 100 parts. Hydrolysis with alcoholic potash converts it into the corresponding acid, which forms granular, yellow crystals and melts at  $150^{\circ}$ . *Ethylic azo- $\beta$ -naphthalenecyanacetate* is precipitated from its potash solution by hydrochloric acid; it melts at  $124^{\circ}$  and dissolves in benzene to the extent of 5.137 parts in 100 parts.

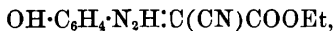
Neither iodine nor sulphurous acid will change the labile form of ethylic tribromophenylhydrazoncyanacetate into the stable form; but a small quantity of iodine will convert the labile form of ethylic  $\alpha$ -naphthylhydrazoncyanacetate into the stable form.

*Ethylic metacarboxyphenylhydrazoncyanacetate*,



was prepared by diazotising metamidobenzoic acid, adding ethylic cyanacetate, and salting out with sodium acetate; it forms crystals which melt at  $222^{\circ}$ . An alcoholic solution of the salt gives precipitates with various metallic salts; these are duly described; the *silver* salt was analysed. An isomeride was not obtained.

*Ethylic hydroxyphenylhydrazonocyanacetates,*



were prepared by diazotising the corresponding amidophenols with amyl nitrite and hydrochloric acid, adding ethylic cyanacetate, and salting out with sodium acetate. The *orthohydroxy*-derivative forms dark brownish-yellow crystals and melts at  $204^{\circ}$ ; the *para*-derivative crystallises in yellow needles and melts at  $150^{\circ}$ ; the *meta*-derivative crystallises in dark, red-brown needles and melts at  $87^{\circ}$ .

*Ethylic sulphophenylhydrazonocyanacetate,*



prepared from diazobenzenesulphonic acid and ethylic cyanacetate, forms yellow crystals, which decompose before they melt, but without explosion; it dissolves freely in water and in dilute alcohol, but not in absolute alcohol, benzene, ether, or chloroform. A *silver* salt was prepared.

A. G. B.

**Isomeric Diazo-derivatives.** By HEINRICH GOLDSCHMIDT (*Ber.*, 1895, **28**, 2020—2027).—The author has examined the depression of the freezing point in solutions of isodiazobenzene potassium and of diazobenzene sodium, a solution of the latter being obtained by the addition of diazobenzene chloride to a solution of soda of known strength and freezing point. The results obtained are analogous to those given by the salts of the syn- and anti-aldoxime salts (this vol., i, 657), and confirm Hantzsch's theory, that these diazo-derivatives are stereo-isomerides, similar to the aldoximes, but do not agree with Bamberger's supposition, that the former has the constitution  $\text{N}:\text{NPh}\cdot\text{OH}$ , and the latter  $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{ONa}$ . In any case, the author regards the first formula as extremely improbable, as the radicle,  $\text{Ph}\cdot\text{N}:\text{N}$ , is a substituted ammonium derivative, and it is extremely unlikely that its hydroxide would possess strongly acid properties.

In the latter portion of the paper, the author proposes a theory of the diazo-compounds which is identical with that just published by Hantzsch (this vol., i, 516), namely, that there are two structurally isomeric classes of diazo-compounds, the first containing the radicle,  $\text{Ph}\cdot\text{N}:\text{N}$ , and the second the true diazo-group,  $\text{Ph}\cdot\text{N}:\text{N}$ , and that the latter are, as Hantzsch has long maintained, capable of existing in two stereoisomeric forms. The reasoning on which these conclusions are based is practically identical with that of Hantzsch in the paper quoted.

H. G. C.

**Action of Halogens and Thiocarbonyl Dichloride on Amidoximes.** By HANS KRÜMMEL (*Ber.*, 1895, **28**, 2227—2233; compare Abstr., 1892, 461).—Benzenylhydrazoximidobenzylidene *hydrobromide* separates from a concentrated solution of benzenylamidoxime in

glacial acetic acid when bromine is added in small quantities until the colour is no longer destroyed. It melts at  $132^{\circ}$ , and when the solution, in water or alcohol, is heated alone or with acids, ammonium bromide and dibenzoylazoxime are formed. The *hydrochloride* is colourless. When excess of bromine is employed in the preparation of the hydrobromide, the *dibromide* of this salt separates as a red powder, which melts at  $132^{\circ}$ ; benzenylhydrazoximidobenzylidene is obtained by treating it with ammonia, and hot alcohol converts it into dibenzoylazoxime.

Parahomobenzenylhydrazoximidoparabromobenzylidene *hydrobromide* is a white, crystalline substance, and melts at  $178^{\circ}$ ; it resembles the foregoing salt in behaviour, and when treated with bromine yields the *dibromide*, which is orange-yellow, and melts at  $135^{\circ}$ .

Metanitrobenzenylhydrazoximidometanitrobenzylidene *hydrobromide* is colourless, and melts at  $158^{\circ}$ ; hot alcohol converts it into *dimetanitrobenzenylazoxime*, which melts at  $138^{\circ}$ . The hydrobromide also yields the *dibromide*, which is yellow, and melts at  $142^{\circ}$ .

*Thiocarbonyldibenzoylamidoxime*,  $\text{CS}(\text{O} \cdot \text{N} \cdot \text{CPh} \cdot \text{NH}_2)_2$ , is obtained by adding thiocarbonyl dichloride to a solution of benzenylamidoxime in benzene; it melts at  $96^{\circ}$ , and decomposes very readily in solution.

*Benzenylazoximethiocarbinol*,  $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{---} \end{smallmatrix} \text{C} \cdot \text{SH}$ , is produced when the solution of the foregoing substance in warm alkali is acidified; it forms white crystals, and melts at  $131^{\circ}$ . The *ethyl* derivative, obtained by digesting the potassium derivative with ethylic iodide, is decomposed by excess of caustic potash, yielding ethylic mercaptan.

*Thiocarbonyldiparahomobenzenylamidoxime* is colourless, and melts at  $115^{\circ}$ . *Parahomobenzenylazoximethiocarbinol* crystallises in white needles, and melts at  $135^{\circ}$ .  
M. O. F.

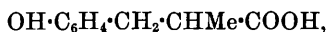
**Tolyl- and Phenyl-anilidophosphonium Derivatives.** By C. A. AUGUST MICHAELIS and FRITZ KUHLMANN (*Ber.*, 1895, **28**, 2212—2217).—*Paratolyltrianilidophosphonium chloride*,  $\text{C}_7\text{H}_7 \cdot \text{P}(\text{NHPh})_3$ , is prepared by heating paratolyltetrachlorophosphine and aniline hydrochloride at about  $200^{\circ}$ ; it is purified by treatment with hydrochloric acid, crystallises in slender, colourless needles, and melts at  $245^{\circ}$ . The *platinochloride*,  $[\text{C}_7\text{H}_7 \cdot \text{P}(\text{NHPh})_3]_2 \text{PtCl}_6$ , is deposited in lustrous, golden plates. The *hydroxide*,  $\text{C}_7\text{H}_7 \cdot \text{P}(\text{NHPh})_3 \cdot \text{OH}$ , obtained by the action of soda on the chloride, is a colourless, crystalline, anhydrous powder, and melts at  $240^{\circ}$ . The *iodide* and *bromide* crystallise in needles melting at  $235^{\circ}$  and  $238^{\circ}$  respectively; the *nitrate* is crystalline, and melts at  $180^{\circ}$ .

*Phenyltrianilidophosphonium chloride*,  $\text{PPhCl}(\text{NHPh})_3$ , is prepared in a similar manner to the tolyl-derivative, which it closely resembles, and crystallises in blue tinted needles melting at  $250^{\circ}$ . The *platinochloride* is deposited in golden, lustrous plates; the *hydroxide* is pulverulent, and melts at  $216^{\circ}$ ; the *bromide* crystallises in colourless, the *iodide* in yellow, needles melting at  $235^{\circ}$  and  $165^{\circ}$  respectively; the *nitrate* forms colourless crystals, and melts at  $160^{\circ}$ .

J. B. T.

**Derivatives of Metahydroxybenzaldehyde.** By G. WERNER (*Ber.*, 1895, **28**, 1997—2002).—When metahydroxybenzaldehyde is boiled with anhydrous sodium phenylacetate and acetic anhydride, it undergoes condensation, yielding *metahydroxystilbenecarboxylic acid*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CPh}\cdot\text{COOH}$ , which crystallises in white, silky needles melting at  $142^\circ$ ; its *silver* salt forms concentric aggregates of needles, which become brown in the light; its *calcium* salt,  $(\text{C}_{15}\text{H}_{11}\text{O}_3)_2\text{Ca} + 2\text{H}_2\text{O}$ , pointed needles; its *barium* salt,  $(\text{C}_{15}\text{H}_{11}\text{O}_3)_2\text{Ba} + 3\text{H}_2\text{O}$ , well developed prisms, and the *ethylic* salt,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{Et}$ , feathery crystals melting at  $183^\circ$ . When heated at about  $240^\circ$ , the acid loses carbonic anhydride, forming *metahydroxystilbene*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHPh}$ , which crystallises in long, thin needles melting at  $180^\circ$ .

With sodium propionate, metahydroxybenzaldehyde yields the corresponding *metahydroxyphenylcrotonic acid*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CMe}\cdot\text{COOH}$ , which forms vitreous plates melting at  $130^\circ$ ; the *silver* salt,  $\text{C}_{10}\text{H}_9\text{O}_3\text{Ag}$ , is a thick, white precipitate, which becomes pink, and finally black, on exposure to light, and the *zinc* salt,  $(\text{C}_{10}\text{H}_9\text{O}_3)_2\text{Zn}$ , a white, flocculent precipitate. When treated with sodium amalgam and water, the acid is reduced to the corresponding *metahydroxyphenylbutyric acid*,



which crystallises in fascicular aggregates of spear-shaped needles melting at  $63^\circ$ .

Attempts were made to bring about the condensation of metahydroxybenzaldehyde and succinic and malonic acids, but without success; metethoxybenzaldehyde, however, also undergoes condensation with the sodium salts of fatty acids, yielding analogous products to the hydroxy-derivative. The ethoxy-derivative may be obtained from the aldehyde, either by the action of potash and ethylic iodide, or by heating it with sodium ethylic sulphate and alkali; it is a yellowish oil, of aromatic odour, which boils at  $245^\circ$ , and soon becomes brown. With sodium acetate and acetic anhydride, it yields *ethylmetacoumaric acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COOH}$ , which crystallises in matted needles and melts at  $122^\circ$ ; with sodium propionate, it yields *metethoxyphenylcrotonic acid*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CMe}\cdot\text{COOH}$ , which forms long, spear-shaped crystals melting at  $80^\circ$ . H. G. C.

**An Isomeric Dichloride of Cinnamic acid.** By CARL T. LIEBERMANN and H. FINKENBEINER (*Ber.*, 1895, **28**, 2235—2247; compare *Abstr.*, 1894, i, 335 and 526).—Cinnamic acid dichloride is usually prepared by passing chlorine into carbon bisulphide or carbon tetrachloride containing cinnamic acid in suspension, the operation being carried on in bright sunlight; it melts at  $167$ — $168^\circ$ . A different product is obtained, however, when the following conditions are observed. Cinnamic acid (60 grams), suspended in carbon tetrachloride (750 grams), is submitted to the action of a current of chlorine (31 grams), the liquid being maintained at the temperature of melting ice, and carefully protected from light; after remaining under these conditions for 8—10 days, solution is complete, and the liquid is transferred to vacuum desiccators provided with soda-lime and paraffin. The viscous oil thus obtained is con-

verted into the *cinchonidine* salt, from which the pure *cinnamic acid dichloride*,  $C_9H_7Cl_2O_2$ , is obtained; it separates in beautiful, rhombic crystals from chloroform to which petroleum has been added; it melts at  $84-86^\circ$ . It is very soluble in chloroform, carbon bisulphide, and carbon tetrachloride; 100 parts of benzene dissolve 43.1 parts at  $21^\circ$ , the same quantity of solvent being required by 2.3 parts of the ordinary dichloride at this temperature. The *methylic salt* is an oil which does not solidify when sown with crystals of methylic cinnamate dichloride (m. p.  $100-101^\circ$ ).

The isomeric cinnamic acid dichloride is dissolved by cold ammonia or soda, chlorocinnamene being formed when the liquid is heated; this decomposition is effected more readily than is the case with ordinary cinnamic acid dichloride, and an alkaline solution of potassium permanganate is also attacked more rapidly, benzoic acid being produced.

The removal of the halogen from cinnamic acid dichloride and its isomeride, or from cinnamic dibromide and allocinnamic dibromide, results in the formation of cinnamic acid, whilst methylic cinnamate is obtained from their methylic salts, and from the methylic salt of the so-called allocinnamic acid dichloride.

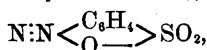
The following crystallographic information is included in the paper. Cinnamic acid dibromide crystallises in colourless plates belonging to the monosymmetric system;  $a : b : c = 0.5472 : 1 : 0.4894$ ;  $\beta = 88^\circ 34.5'$ . Cinnamic acid dichloride (m. p.  $167-168^\circ$ ) belongs to the monoclinic system;  $a : b : c = 0.2445 : 1 : 0.3485$ ;  $\beta = 77^\circ 59'$ . The isomeride forms rhombic crystals;  $a : b : c = 0.8114 : 1 : 1.3611$ . The dibromide of methylic cinnamate crystallises in monoclinic plates;  $a : b : c = 0.91428 : 1 : 1.47985$ ;  $\beta = 83^\circ 1'$ . The dibromide of the ethylic salt is monosymmetric;  $a : b : c = 0.5541 : 1 : 0.8000$ ;  $\beta = 88^\circ 54'$ . The dichloride of methylic cinnamate is isomorphous with the dibromide;  $a : b : c = 0.89585 : 1 : 1.4278$ ;  $\beta = 81^\circ 23.5'$ .

M. O. F.

**Diazosulphanilic acid and its Stereoisomeric Salts.** By ARTHUR HANTZSCH and D. GERILOWSKI (*Ber.*, 1895, **28**, 2002—2012).—This paper contains a detailed account of the investigation of diazosulphanilic acid and its salts, some of the results of which have already been mentioned by Hantzsch, in his recent paper on diazonium compounds (this vol., i, 516). Diazosulphanilic acid has not the constitution usually assigned to it, namely,



but, like all other diazo-compounds which are stable in acid solution, is in reality a diazonium compound, having the constitution,



and is the neutral anhydride of the diazoniumsulphonic acid. From the molecular weight in aqueous solution, it is shown that the above is the molecular formula.

When diazosulphanilic acid is treated with soda under certain

conditions of concentration and below  $0^{\circ}$ , it is converted into sodium syndiazobenzenesulphonate,  $\begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} \\ || \\ \text{N} \cdot \text{ONa} \end{smallmatrix}$ , which forms white,

silky needles, containing  $4\text{H}_2\text{O}$ ,  $3\frac{1}{2}$  mols. of which are evolved when it is kept over sulphuric acid or phosphoric anhydride; it rapidly reddens on exposure to air, but is perfectly stable if kept over calcium chloride. Its aqueous solution has a strongly alkaline reaction; it unites with alkaline  $\beta$ -naphthol with great readiness, and loses the whole of its nitrogen on warming in a current of carbonic anhydride. It also gives an intense yellow coloration with ammonia, and turns the skin orange, or dark red. When heated quickly with a small quantity of water, it is converted into the stereoisomeric sodium antidiazobenzene-sulphonate,  $\begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na} \\ || \\ \text{ONa} \cdot \text{N} \end{smallmatrix}$ , already obtained by Bamberger, and

supposed by him at first to be a nitrosamine derivative; it forms nacreous plates, contains no water of crystallisation, only gives a slight coloration with  $\beta$ -naphthol, and does not affect the skin. The conversion of the syn- into the anti-salt also takes place slowly at the ordinary temperature in aqueous solution, but the solid syn-salt may be kept many weeks in an exsiccator without alteration. The syn-potassium salt is obtained in the same manner as the sodium salt, and appears to be anhydrous, but gradually changes into the anti-salt, even in the solid state. Both the syn- and anti-salt lose nitrogen when boiled with water, the elimination being complete with the former, and nearly so with the latter.

In order to prove that these two salts are in reality both true diazo-compounds, the degree of dissociation and number of ions in their aqueous solutions was determined, and found to be three in both cases, whereas if either of the salts was a diazonium derivative, the number of ions must have been at least four. Both salts being therefore diazo-compounds, they must be regarded as stereoisomerides.

An indirect proof of the intramolecular change which takes place in the formation of syndiazobenzene salts from diazosulphanilic acid is found in the action of alkalis on the latter. When slightly less than an equivalent of alkali is added to a solution of diazo-sulphanilic acid, at  $0^{\circ}$  and quite neutral, the reaction of the mixture becomes strongly alkaline, but after a time the solution gradually becomes neutral again, without any evolution of nitrogen. The first addition of alkali causes the formation of the salt still containing the free diazonium radicle, which has an alkaline reaction, but this gradually undergoes an intramolecular change into the diazo-group forming the neutral salt,  $\text{ONa} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ . Conversely, if acid be added to the syn-diazo salt,  $\text{ONa} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ , the solution becomes neutral as soon as it is completely converted into the salt,  $\text{OH} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ ; on the further addition of acid, the solution assumes an acid reaction, but after a few minutes again becomes neutral, owing to the formation of the diazonium group, which is the only form capable of existing for any length of time in acid solution.

H. G. C.

**Diphenacylacetic acid and its Reduction Products.** By AUGUST PUSCH (*Ber.*, 1895, **28**, 2102—2106).—The acid obtained by Sattler (*Abstr.*, 1893, i, 389) from chloralacetophenone by treatment with hot sodium carbonate solution is identical with the diphenacylacetic acid prepared by Kues and Paal (*Ber.*, **19**, 3147). On reduction with sodium amalgam, this acid is converted into 3:4-dihydroxy-diphenylpentamethylene-1-carboxylic acid,  $\text{COOH}\cdot\text{CH} < \begin{matrix} \text{CH}_2\cdot\text{CPh}\cdot\text{OH} \\ \text{CH}_2\cdot\text{CPh}\cdot\text{OH} \end{matrix}$ ,

which crystallises in needles, and melts and decomposes at about  $200^\circ$ . This acid, which is insoluble in cold benzene, is accompanied by an isomeric acid, which is readily soluble in benzene, and melts at  $162$ — $164^\circ$ . This second acid is probably an allo-form of that first described. Each of these forms, when heated with hydriodic acid and phosphorus, yields the same two isomeric 3:4-diphenylpentamethylene-carboxylic acids. One of these crystallises in nodular aggregates, melting at  $186$ — $187^\circ$ , whilst the other, which the author names the *allo-acid*, is remarkably soluble in cold benzene, and melts at  $150$ — $152^\circ$ .

Three stereo-isomerides of the acid in question are possible, and the exact constitution of the two forms which have been obtained has not yet been ascertained. A. H.

**A Brominated Bye-product of the Preparation of Diphenacylacetic acid from Bromacetophenone.** By AUGUST PUSCH (*Ber.*, 1895, **28**, 2106—2107; compare the foregoing abstract).—The brominated bye-product obtained in the preparation of diphenacylacetic acid from bromacetophenone and ethylic sodiomalonate crystallises in silky needles, melting at  $159$ — $160.5^\circ$ , and has the molecular formula,  $\text{C}_{18}\text{H}_{15}\text{BrO}_3$ . It appears to contain a keto-carbonyl group, but its constitution has not yet been ascertained. A. H.

**Condensation of Orthotoluidine with  $\alpha$ -Diketones and with the Salts of  $\alpha$ -Ketonic acids.** By VICTOR KULISCH (*Monatsh.*, 1895, **16**, 351—357; compare *Abstr.*, 1894, i, 552).—Benzoylbenzylidenetoluidine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{CPhBz}$ , obtained on condensation of benzile with orthotoluidine, crystallises from ether in beautiful rhombs [ $a:b:c = 0.45644:1:0.63358$ ], is readily soluble in benzene, chloroform, and hot water, melts at  $103$ — $104^\circ$ , and is reconverted by acids into its generators. It yields an *oxime*,  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$ , which crystallises in slender, white needles, dissolves readily in alcohol, and melts at  $178$ — $180^\circ$ .

2:2'-Hydroxymethylquinoline,  $\text{C}_{10}\text{H}_9\text{NO}$ , obtained on condensation of orthotoluidine with ethylic pyruvate, crystallises from hot alcohol in slender, white needles, melts at  $203$ — $205^\circ$ , has an aromatic odour, and is only sparingly soluble in water. On distillation with zinc-dust, it yields a red oil, which boils at  $239$ — $255^\circ$ , has the odour of quinaldine, and gives a platinochloride,  $(\text{C}_9\text{NH}_6\text{Me})_2\text{H}_2\text{PtCl}_6$ , which melts at  $226$ — $230^\circ$ . The base is therefore 2:2'-hydroxymethylquinoline, which forms a *platinochloride*, melting at  $225$ — $228^\circ$ , a *sulphate*, melting at  $86$ — $87^\circ$ , and a *picrate*, melting at  $95$ — $96^\circ$ .

G. T. M.



**Basic Properties of the Rosanilines and their Derivatives.**

By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], 13, 427—430).—In reply to Prud'homme (this vol., i, 423), the author reiterates the view he has held for the past 15 years as to the constitution of the rosanilines, namely, that they all contain electropositive univalent radicles of the type,  $C(C_6H_4 \cdot NH_2)_3$ , in combination with chlorine, hydroxyl, &c., and that in the dyes themselves these radicles are combined with such electronegative radicles as chlorine, the corresponding carbinols being colourless. The introduction of sulphonic groups into the phenyl radicles has practically no effect on their basic properties. These views are in reality confirmed by Prud'homme's results.

JN. W.

**Constitution of the Rosanilines.** By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [3], 13, 431—433).—Prud'homme's view that the rosaniline carbonates are ammonium rather than ethereal salts is inconsistent with the adoption of the author's formula,  $CCl(C_6H_4 \cdot NH_2)_3$ , for the hydrochloride. The fact is that the character of the triphenylcarbinol derivatives varies over a very wide range. Triphenylchloromethane, for example, is hydrolysed by cold water, and thus resembles the acid chlorides in character, whereas triamidotriphenylcarbinol is more basic than ammonia. But triphenylcarbinol forms alkylic ethers as stable as the mixed aliphatic ethers, and is thus still distinctly alcoholic in nature, although its basic character is not sufficiently marked to allow of the formation of salts with acids; triamidotriphenylcarbinol, on the other hand, forms both ethers with alkylic radicles, and ethereal salts with acid radicles. Thus even the most acid in character of the rosaniline group is distinctly alcoholic, and Prud'homme's carbonate must be regarded as a true ethereal salt.

JN. W.

**Corallin and Rosaniline.** By CARL ZULKOWSKI (*Monatsh.*, 1895, 16, 358—403).—Dyes and other organic compounds having a phenolic character may be conveniently purified by precipitating their alkaline solutions with carbonic anhydride. The method answers well for aurin, roseol, and their derivatives, for pnenolphthaleïn, and other similarly constituted substances. Corallin, when prepared from pure phenol, contains two dyes in addition to aurin; these have the formulæ  $C_{20}H_{16}O_4$  and  $C_{22}H_{16}O_5$  (?) respectively, and do not appear to be closely related to each other. Corallin thus obtained also contains two substances which are isomeric but they exhibit no tinctorial properties; they contain 1 atom more of oxygen than aurin, have the formula  $C_{19}H_{14}O_4$ , and may be regarded as  $\alpha$ - and  $\beta$ -aurin oxide respectively. When corallin is prepared from phenol containing orthocresol, in addition to the products mentioned above, the following series of compounds may be isolated:  $C_{21}H_{20}O_4$ ,  $C_{22}H_{18}O_4$ ,  $C_{20}H_{16}O_4$ ,  $C_{20}H_{10}O_5$ ; the first of these is roseol, the others have not previously been isolated. On diazotising rosaniline which is free from the para-compound, the substances  $C_{25}H_{22}O_4$  (methyloseol) and  $C_{23}H_{20}O_4$  may be obtained.

G. T. M.

**Theory of Dyeing. Distribution of Methylene-Blue between Water and Mercerised Cellulose.** By GEORG V. GEORGIEVICS and ERNST LÖWY (*Monatsh.*, 1895, **16**, 345—350).—It has been previously shown (compare Georgievics, this vol., ii, 259) that the expression  $\sqrt{x}$ /dye remaining in bath dye taken up by fibre, where  $x$  expresses the measure of the affinity of the dye for the fibre, is a constant for most, if not for all, substantive colours. The authors find that the same expression holds good in the distribution of methylene-blue between water, and cellulose which has been treated with caustic soda (mercerised cellulose), and that it is independent of the structure of the cellulose, which may be fibrous, or in the pulverulent form as obtained on adding an acid to a solution of cellulose in ammoniacal cuprous oxide. It appears, moreover, that the quantity of dye taken up at different temperatures depends on the structure of the cellulose in a definite way, and that a far-reaching analogy exists between dyeing and other absorption phenomena. G. T. M.

**Isomeric Naphthalene Derivatives.** By PAUL FRIEDLAENDER (*Ber.*, 1895, **28**, 1946—1953).—Witt's acetyl-1-naphthol (*Abstr.*, 1888, 486) is shown to have the properties of 2-acetyl-1-naphthol; it yields *ethylic* and *methylc ethers* only with difficulty. The former of these is an oil boiling at about 320°, and yielding a *phenylhydrazone*, which melts at 117°. Acetyl naphthol yields a hydrazine derivative melting at about 165°. With sulphuric acid, it yields 2-acetyl-1-naphthol-4-sulphonic acid, the barium salt of which crystallises with 5H<sub>2</sub>O; this acid, when treated with dilute nitric acid, is converted into yellow 4:2-nitroacetyl-1-naphthol, which melts at 157°, and forms a red *phenylhydrazone* melting at 221°. This nitro-compound is reduced by stannous chloride to 4:2-amidoacetyl-1-naphthol, a reddish-brown substance, of which the *platinochloride* and *acetyl derivative*, melting at 107°, were prepared, and which, when treated with bleaching powder, yields yellowish-brown *acetylnaphthaquinone chlorimide* melting at 137°, and, when oxidised with ferric chloride, a yellow *acetylnaphthaquinone*, which melts and decomposes at 78°.

1:3-Naphthylaminesulphonic acid was prepared from the 1:3:1'-amidodisulphonic acid by reducing the latter with sodium amalgam or heating it with 75 per cent. sulphuric acid; its *barium salt* crystallises with H<sub>2</sub>O; it can be hydrolysed to 1:3-naphtholsulphonic acid. When fused with potash, it yields yellow 1:3-amidonaphthol, which decomposes at 185°, yields a *monacetyl derivative* melting at 179°, and, when heated with strong aqueous ammonia at 150°, is converted into 1:3-naphthylenediamine. This substance melts at 96°, and its *diacetyl derivative* at 263°; it has not been properly described before, and it is interesting as completing the list of the possible naphthylenediamines, all of which are now well characterised. C. F. B.

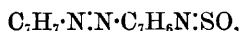
**Naphthazarin from 1:2:1':4'-Tetranitronaphthalene (δ).** By WILHELM WILL (*Ber.*, 1895, **28**, 2234—2235; compare this vol., i, 235 and 477).—When δ-tetranitronaphthalene is reduced with tin

and hydrochloric acid, naphthazarin is produced, and at the same time a substance is formed which crystallises in plates with a bronze lustre; probably this compound is amidodiimidonaphthol (*Ber.*, 1878, 11, 1661). M. O. F.

**Preparation of Anhydrous Diazo-Salts.** By EMIL KNOEVENAGEL (*Ber.*, 1895, 28, 2048—2060; compare *Abstr.*, 1891, 54).—By means of the process already described (*loc. cit.*), the author has prepared the following salts. The diazo-sulphates of  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine, the diazo-chlorides of orthotoluidine,  $\alpha$ -naphthylamine, and  $\beta$ -naphthylamine, the diazo-nitrates of paranisidine,  $\alpha$ -naphthylamine, and  $\beta$ -naphthylamine, and the diazo-oxalates of aniline, paratoluidine, paranisidine, and paraphenetidine. Further particulars are also given regarding those salts which have already been obtained in the anhydrous state (*loc. cit.*). M. O. F.

*Note by Abstractor.*—Anhydrous  $\beta$ -diazonaphthalene chloride was prepared by Möhlau and Berger (*Ber.*, 1893, 26, 2000).

**Thionylamines of Amidazo-derivatives and of Naphthylene-diamines.** By C. A. AUGUST MICHAELIS and G. ERDMANN (*Ber.*, 1885, 28, 2192—2204).—*Thionylparazorthoamidotoluene*,



is prepared from parazorthoamidotoluene hydrochloride [ $\text{Me} : \text{N} = 1 : 2$ ;  $\text{NH}_2 : \text{Me} : \text{N} = 1 : 2 : 4$ ] and thionyl chloride, in benzene solution; it crystallises in golden needles, melts at  $89^\circ$ , evolves sulphurous anhydride in moist air, is slowly decomposed when boiled with water or alcohol, more rapidly with acids, and immediately with alkalis. All these solutions colour the skin intensely yellow. The isomeric compound from parazorthoparamidotoluene hydrochloride, [ $\text{Me} : \text{N} = 1 : 4$ ;  $\text{NH}_2 : \text{Me} : \text{N} = 1 : 2 : 4$ ] melts at  $86^\circ$ , and is deposited from benzene in small, steel-blue needles, from light petroleum in broad needles with a light bluish-brown lustre. In its properties, it resembles the preceding compound.

Benzeneparazonaphthylamine,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{NPh}$  [ $\text{NH}_2 : \text{N} = 1 : 4$ ], has been previously prepared by Griess; Bamberger and Schieffelin described the hydrochloride under this name; it melts at  $123^\circ$ , and gives bluish-red solutions which become pure red with acids and yellow with alkalis. The *acetyl* derivative crystallises in yellow plates, and melts at  $233^\circ$ . The *benzoyl* derivative forms brownish needles melting at  $201^\circ$ . The free base readily yields a *thionyl* derivative, but the hydrochloride reacts less easily; it crystallises in dark orange-red needles, melts at  $136^\circ$ , and resembles the above toluene compounds.

*Thionyl- $\alpha$ -naphthylazo- $\alpha$ -naphthylamine*,  $\text{C}_{10}\text{H}_7\cdot\overset{1}{\text{N}}\cdot\overset{4}{\text{N}}\cdot\text{C}_{10}\text{H}_6\cdot\overset{1}{\text{N}}\cdot\text{SO}$ , prepared from the corresponding naphthyl-naphthylamine, is brown and pulverulent, and melts at  $156$ — $157^\circ$ . *Thionylorthoazoparamidotoluene*, [ $\text{N} : \text{NSO} = 1 : 2$ ], is prepared from the amide, and is deposited in brownish-red crystals melting at  $95$ — $105^\circ$ . It is somewhat unstable, and when heated at  $170^\circ$  (30 mm.) is resolved into the pseudoazimide,

$C_7H_6 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > NC_7H_7$ , sulphur and sulphurous anhydride. This reaction indicates that orthoazamidotoluene is not a closed chain or quinoid<sup>al</sup> compound, but has the ordinary open chain formula.

By the interaction of thionyl chloride and benzeneorthoazo- $\beta$ -naphthylamine, benzenepseudoazimidonaphthylene, sulphur, sulphurous anhydride, and, in small quantity, impure thionylamine are formed. *Naphthalenepseudoazimidonaphthalene*,  $C_{10}H_6 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > N, C_{10}H_7$  [ $N : N = 1 : 2$ ;  $N = 2$ ], is formed, when thionyl chloride reacts with  $\beta$ -naphthylorthoazo- $\beta$ -naphthylamine; it crystallises in colourless needles, and melts at  $186^\circ$ . No thionyl derivative could be obtained.

1 : 4-*Thionynaphthylenediamine*,  $C_{10}H_6(N:SO)_2$ , prepared from thionyl chloride and naphthylenediamine hydrochloride, crystallises in lustrous, light-brown needles, and melts at  $126^\circ$ ; it is slowly decomposed when boiled with water or alcohol, more rapidly by the addition of acids, and immediately by alkalis. Thionyl chloride and ortho-naphthylenediamine yield naphthylpiazthiole,  $C_{10}H_6 < \begin{smallmatrix} N \\ \parallel \\ N \end{smallmatrix} > S$ .

J. B. T.

**Para-substituted Derivatives of  $\alpha$ -Naphthoic acid.** By PAUL FRIEDLAENDER and J. WEISBERG (*Ber.*, 1895, 28, 1838—1843).—The following substances were prepared in the course of an unsuccessful attempt to obtain an anhydride of tetrahydroparamidonaphthoic acid. 1 : 4-*Nitronaphthonitrile*, prepared from nitronaphthylamine by means of the diazo-reaction, crystallises in colourless needles which melt at  $133^\circ$  and are free from odour. The corresponding *amidonaphthonitrile* melts at  $174^\circ$ , is odourless, and forms crystalline salts. The *acetyl* derivative forms needles melting at  $189.5^\circ$ . 1 : 4-*Chloronaphthonitrile*, prepared from the amido-compound by Sandmeyer's reaction, crystallises in long white needles melting at  $110^\circ$ . *Nitronaphthamide*,  $NO_2 \cdot C_{10}H_6 \cdot CO \cdot NH_2$ , prepared by the action of hydrogen peroxide on the nitrile in the presence of alcoholic potash (Radziszewski's method), melts at  $218^\circ$ . Both the nitrile itself and the amide are very stable to the ordinary hydrolytic reagents, but may be converted into the acid by boiling aqueous baryta. 1 : 4-*Nitronaphthoic acid* forms faintly yellow needles melting at  $220^\circ$ ; it is sparingly soluble in hot water, and forms soluble salts of the alkali metals. The *ethylic salt* crystallises in yellow needles, and melts at  $54^\circ$ . *Amidonaphthamide* forms white needles, which melt at  $175^\circ$ , after previously undergoing decomposition; it is easily decomposed by acids with formation of naphthylamine, but is converted by alcoholic potash at  $130$ — $140^\circ$  into *amidonaphthoic acid*. This acid is, however, best prepared by the reduction of nitronaphthoic acid; it is moderately soluble in hot water, and forms brownish needles melting at  $177^\circ$ . It readily decomposes when dissolved in hydrochloric acid, carbonic anhydride being evolved and naphthylamine formed when the liquid is allowed to remain. 1 : 4-*Chloronaphthoic acid* crystallises in white needles, melting at  $210^\circ$ ; it is not acted on by ammonia at  $200^\circ$ , or by ammonium carbonate at  $220^\circ$ .

A. H.

**Analyses of Cotton Dyed with Alizarin.** By CARL T. LIEBERMANN and PAUL MICHAELIS (*Ber.*, 1895, **28**, 2264—2265; compare this vol., i, 108).—The authors give analyses of samples dyed with dark Krapp-red, dark violet, and dark claret; the dyeing being continued, in each case, until the deepest shade was attained. It was found that the proportion of dye to mordant was considerably greater than in all previous cases, thus indicating that the whole of the mordant was dyed. J. J. S.

**Derivatives of Anthracene- $\beta$ -sulphonic acid and Anthracyl Hydrosulphide.** By WERNER HEFFTER (*Ber.*, 1895, **28**, 2258—2264).—*Anthracene- $\beta$ -sulphonic chloride*,  $C_{14}H_9SO_2Cl$ , obtained by heating an intimate mixture of the sodium salt and phosphorus pentachloride with equal parts of phosphorus oxychloride and acetic acid, melts at  $122^\circ$ , and is very stable in the presence of cold water. When oxidised with chromic acid, it yields anthraquinonesulphonic chloride. The *anide*,  $C_{14}H_9SO_2NH_2$ , melts at  $261^\circ$ , is insoluble in ether, alcohol, acetic acid, and benzene, but is soluble in nitrobenzene and in phenol. The *anilide* forms glistening plates, which melt at  $201^\circ$ . The *dimethylanilide*, obtained by acting on the chloride with dimethylaniline, melts at  $165^\circ$ . The *phenylhydrazide*,  $C_{14}H_9SO_2NH\cdot NHPH$ , melts at  $210^\circ$ .

*Tetrabromanthracenesulphonic chloride* is obtained by the action of bromine vapour on the chloride; it is a greenish-yellow powder, melts at  $125^\circ$ , and is readily soluble in benzene, acetic acid, and chloroform.

*Sodium tetrabromanthracenesulphonate*,  $C_{14}H_9Br_4\cdot SO_3Na + 4H_2O$ , is a yellow powder readily soluble in warm water.

*Methylic anthracenesulphonate*, prepared by Krafft and Roos' method (*Ber.*, **25**, 2255, and **26**, 2823), forms yellow plates, melts at  $157^\circ$ , and dissolves in alcohol, ether, and benzene to a blue fluorescent solution. The *ethylic salt* melts at  $160^\circ$ .

*Methylic anthraquinonesulphonate*,  $C_{14}H_7O_2\cdot SO_3Me$ , melts at  $123^\circ$ , and is converted by water or alcohol into the acid. The corresponding *ethylic salt* melts at  $125^\circ$ .

*Anthracenesulphinic acid*,  $C_{14}H_9\cdot SO_2H$ , prepared by acting on the sulphonic chloride with zinc and water, or sodium sulphite, forms greenish plates. The *silver salt* is obtained as a white, flocculent precipitate.

*$\beta$ -Anthracyl hydrosulphide*,  $C_{14}H_9\cdot SH$ , may be prepared by the methods of Vogt (*Annalen*, **119**, 142), Schiller (*Ber.*, **10**, 939), and Märker (*Annalen*, **136**, 78). It crystallises from benzene in pale yellow needles, decomposes at  $220^\circ$ , and is odourless. The *mercuriochloride* compound forms a canary-yellow precipitate, which is decomposed by warm hydrochloric acid into the mercaptan and mercuric chloride. J. J. S.

**Diphenylanthrone.** By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1895, **121**, 102—106).—When the phthalic tetrachloride melting at  $88^\circ$  is dissolved in four parts of benzene free from thiophen, and mixed with 3.5 parts of dry aluminium chloride, the

temperature being kept at 40°, it yields *diphenylanthrone*. With other proportions of aluminium chloride, phenyloxanthranol and anthraquinone are formed. It follows from the production of these compounds that, unless molecular transpositions are assumed to take place, the phthalic tetrachloride melting at 88° is unsymmetrical, and has the constitution  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ .

Diphenylanthrone is also obtained by the condensation of benzene with phenyloxanthranol in presence of sulphuric acid, and is probably identical with the product obtained by Baeyer under these conditions, but not described by him; it is also formed by the action of benzene and aluminium chloride on *phenyloxanthranol chloride*. The latter is obtained by heating at 140—150° a mixture of diphenylphthalide and phosphorus pentachloride in molecular proportion, and crystallises in white prisms melting at 164° (uncorr.).

Diphenylanthrone can also be obtained by the action of benzene and aluminium chloride on anthraquinone dichloride (dichloranthrone). There would seem to be no doubt that its constitution is  $\text{CPh}_2\langle\text{C}_6\text{H}_4\rangle\text{CO}$ . Whatever the mode of formation, it crystallises in colourless, very brilliant needles melting at 192°, insoluble in water and almost insoluble in alcohol, ether, or light petroleum, but soluble in boiling benzene or glacial acetic acid. Cryometric determinations show that its molecular weight is 346. Notwithstanding the presence of the CO-group, it combines neither with hydroxylamine nor with phenylhydrazine.

C. H. B.

**Isomerism in the Terpene Series.** By OTTO WALLACH (*Ber.*, 1895, **28**, 1955—1967).—The study of carvenone and isothujone has been repeated, and the results agree with those obtained earlier (*Annalen*, **286**, 102). The ketones studied were isolated by means of their semicarbazide compounds (compare Baeyer, this vol., i, 536); the latter were usually obtained in two modifications with different melting points; that melting at the higher temperature being referred to as the  $\alpha$ -modification. The substances described were all obtained in a very pure state; their physical constants are enumerated below, *d* standing for specific gravity,  $n_D$  for index of refraction, and *M* for molecular refraction.

Melting-points of	Semicarbazone.		Oxime.
	$\alpha$ .	$\beta$ .	
Isothujone .....	208—209°	184—185°	119—120°
Carvotanacetone .....	177—178	—	92—93
Carvenone .....	200—201	153—154	91°
Thujamenthone .....	179°	—	95—96°
Tetrahydrocarvone .....	173—174°	135—140°	105°

	Boiling-point.	<i>d.</i>	<i>n</i> <sub>D</sub> .	M.	
$C_{10}H_{16}O$ .	Thujone . . . . .	200—201°	0·917	1·4511	44·61
	Dihydrocarvone . . . . .	221—222	0·927	1·4717	45·84
	Carvenone . . . . .	232—233	0·927	1·4822	46·76
	Isothujone . . . . .	231—232	0·927	1·4822	46·76
	Carvotanacetone . . . . .	228—229	0·932	1·4793	46·27
	Pulegone . . . . .	221—222	0·936	1·4846	46·51
$C_{10}H_{18}O$ .	Tetrahydrocarvone (dihydrocarvenone) . . . . .	220—221°	0·904	1·4554	46·55
	Thujamenthone . . . . .	208—209	0·891	1·4471	46·19
	Menthone . . . . .	208°	0·894	1·4406	46·25

The calculated values of M are as follows (a double linking being denoted by [=]).

Ketone, $C_{10}H_{16}O$ .	Alcohol, $C_{10}H_{16}OH$ [=.	Ketone, $C_{10}H_{16}O$ [=.	Alcohol, $C_{10}H_{16}OH$ [=2.	Ketone, $C_{10}H_{18}O$ .
44·11	45·05	45·82	46·76	46·21

Dihydrocarvone has the physical characters of an unsaturated, thujone that of a saturated, ketone. When treated with dilute sulphuric acid, they are converted into isomeric substances, carvenone and isothujone respectively; these have an identical physical character—that of an alcohol with two ethylene linkings, but their chemical character is that of a ketone with one ethylene linking; an anomaly of the same kind is exhibited by pulegone. Carvenone and isothujone are converted by reduction into the alcohols tetrahydrocarveol and thujamenthol,  $C_{10}H_{20}O$ , and these, on oxidation, yield tetrahydrocarvone and thujamenthone.

Thujone (tanacetone) is further converted at 280° into carvotanacetone; this already differs from isothujone, and when it is reduced to a tetrahydro-derivative (alcohol), and the latter is oxidised, a substance is obtained which is identical with tetrahydrocarvone, and different from thujamenthone. Thujone is thus converted by heat into a different isomeride from that into which dilute sulphuric acid transforms it.

C. F. B.

**Alcohols derived from a Dextro-rotatory Terpene, Eucalyptene.** By GUSTAVE BOUCHARDAT and TARDY (*Compt. rend.*, 1895, 120, 1417—1420).—Eucalyptene, the dextrogyrate terpene of eucalyptus, has a specific rotatory power of  $[\alpha]_D = +39$  at 15°; in boiling point (156—157°) and sp. gr. (0·870 at 0° and 0·865 at 18°), it is identical with the lævogyrate terpene from the pine oil of Landes. When heated with glacial formic acid, it yields a terpinol,  $C_{20}H_{32}O$ , which has a peculiar odour of lilac, crystallises from ether in bulky crystals melting at 33—34°, boils and decomposes at about 218°, and otherwise resembles the terpinol from the lævogyrate terpene, but its specific rotatory power  $[\alpha]_D = +88°$ .

When heated with benzoic acid at 150°, eucalyptene yields a

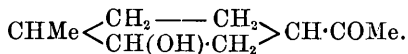
borneol which melts and boils at about  $213^{\circ}$ . Its rotatory power  $[\alpha]_D = +18^{\circ} 40'$ , whilst that of the corresponding camphor is  $+31^{\circ}$ , and hence the ratio between the two is abnormal, and indicates the presence of the isomeride with reversible rotatory power described by Montgolfier. In fact, by repeated conversion into the benzoate, the specific rotatory power of the borneol can be raised to  $+25^{\circ} 50'$ , whilst that of the camphor formed from it remains constant at  $+31^{\circ}$ . The camphor, when oxidised with nitric acid, yields a mixture of ordinary camphoric acid, which is somewhat soluble in water, melts at  $181^{\circ}$ , and has a specific rotatory power of  $+44^{\circ}$ , and racemocamphoric acid which is only slightly soluble in water, melts at  $203\text{--}204^{\circ}$ , and yields an anhydride which melts at  $223^{\circ}$ . The borneol seems consequently to be a mixture of dextrogyrate borneol with some normal lævogyrate borneol and the lævogyrate borneol of Montgolfier, with variable rotatory power.

The isoborneol or fenchol,  $C_{10}H_{14}O_2$ , obtained at the same time as the borneol melts at about  $45^{\circ}$ , boils at  $198\text{--}200^{\circ}$ , and has all the properties of the isoborneol from the lævogyrate terpene, except that its specific rotatory power is  $-10^{\circ}$  to  $-10^{\circ} 20'$ . The corresponding camphor is strongly dextrogyrate, liquid at  $15^{\circ}$ , and solid at  $0^{\circ}$ , and seems to be identical with the anisic camphor of Landolph or the fenchone of Wallach.

The inactive eucalyptene seems to be a true racemic hydrocarbon; it yields racemic borneol, inactive camphor, racemic camphoric acid melting at  $203\text{--}204^{\circ}$ , and the racemic camphoric anhydride melting at  $223^{\circ}$ . It also yields an inactive isoborneol, a liquid racemic camphor, and an inactive terpinol, which seems to be identical with the terpinol from terpin.

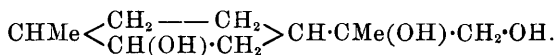
C. H. B.

**Oxidation of Dihydrocarveol and of Limonene.** By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 2141—2150).—By treating the trihydroxyhexahydrocymene, obtained by the oxidation of dihydrocarveol (Wallach, *Annalen*, **277**, 151), with a mixture of chromic anhydride and sulphuric acid, the authors have obtained a substance which, from its reactions, they consider to be 3 : 1 : 6-acetylhydroxymethylhexamethylene,



It is an oil which distils at  $155\text{--}156^{\circ}$  under a pressure of 22 mm., and apparently yields a mixture of two oximes, one of which melts at  $128^{\circ}$ . When treated with an alkaline solution of bromine, it gives *metahydroxyhexahydroparatoluic acid*; this melts at  $153^{\circ}$ , decomposes sodium carbonate, yields a sparingly soluble silver salt, and a phenylurethane derivative which melts at  $193\text{--}194^{\circ}$ . When treated with bromine at  $190^{\circ}$ , the acid is converted into a mixture of *metahydroxyparatoluic acid* and *paratoluic acid*. The authors think that these facts point to the following constitutions.

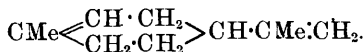
Trihydroxyhexahydrocymene from dihydrocarveol,





Dihydrocarveol,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$ . Carvone,

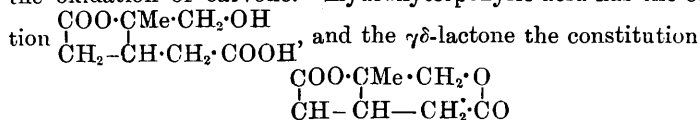
$\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CMe} \cdot \text{CH}_2$ . Limonene,



All these substances are optically active, and contain an asymmetric carbon atom.

Dihydrocarvone, when treated according to Wagner's method, and then further oxidised with chromic anhydride, yields a diketone,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{COMe}$ , which distils at 152—160° under a pressure of 22 mm. It yields two isomeric *dioximes*, one of which melts at 197—198°, and the other at 175—176°.

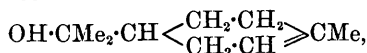
The authors give constitutional formulæ for the products obtained by Best (Abstr., 1894, i, 361) and by Wallach (Abstr., 1894, i, 421) on the oxidation of carvone. Hydroxyterpenylic acid has the constitution



Oxidation experiments with limonene are being continued; the results already obtained agree with the formula for limonene given above.

J. J. S.

**Optically Active Terpeneol.** By FRIEDRICH W. SEMMLER (*Ber.*, 1895, **28**, 2189—2191).—By the substitution of hydroxyl for chlorine, limonene hydrochloride is converted into active *terpeneol*,



which boils at 215°, and has an odour of hawthorn blossom and lilac; its optical activity is of the same sign as that of the limonene derivative.

J. B. T.

**Bromophenylhydrazone and Semicarbazone of d-Camphor.** By FERDINAND TIEMANN (*Ber.*, 1895, **28**, 2191—2192).—*d*-Camphor-*parabromophenylhydrazone*,  $\text{C}_{10}\text{H}_{16} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ , is prepared by the interaction of camphor and parabromophenylhydrazine in concentrated acetic acid solution, at the ordinary temperature; it crystallises in pale yellow plates, melts at 101°, and gradually darkens on exposure to air. The corresponding *semicarbazone*,  $\text{C}_{10}\text{H}_{16} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , forms colourless needles melting at 236—238°.

J. B. T.

**Campholene Derivatives.** By FERDINAND TIEMANN (*Ber.*, 1895, **28**, 2166—2189).—The formulæ previously assigned to a number of campholene derivatives (this vol., i, 426) require amendment in respect to the position of the ethylene linking, the formulæ given for the  $\alpha$ -compounds are actually those of the  $\beta$ -series, and *vice versa*.

$\alpha$ -Campholenonitrile is converted into  $\beta$ -campholenonitrile by the prolonged action of strong acids, hydriodic acid acting the most readily. *d*-Camphoroxime, however, may be recrystallised from moderately concentrated hydrochloric acid without change.

$\alpha$ -Campholenamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH} < \begin{smallmatrix} \text{CH}_2-\text{CH} \\ \text{CMe}_2\cdot\text{CMe} \end{smallmatrix}$ , is formed when the nitrile is hydrolysed by alcoholic potash or when it is fused with potassium hydroxide; it is also obtained by the dehydration of ammonium  $\alpha$ -campholenate; it readily crystallises, melts at  $130^\circ$ , is laevogyrate, and is converted into  $\beta$ -campholenamide by the action of mineral acids. Isoamidocamphor is formed by the action of mineral acids on either of the nitriles or amides, but when these are hydrolysed by means of alcoholic potash,  $\alpha$ - and  $\beta$ -campholenic acids are obtained; the former is an oil, and boils at  $251\text{--}255^\circ$  under atmospheric pressure, and at  $142\text{--}144^\circ$  at 10 mm.;  $\beta$ -campholenic acid boils at  $245^\circ$ .

Dihydrocampholenolactone boils at about  $260^\circ$ ; when quite free from campholenic acids, it may be distilled under reduced pressure without decomposition, it then crystallises, and melts at  $25\text{--}30^\circ$ ; the lactone is best freed from the acids by repeatedly treating it, in ethereal solution, with ammonia. Isohydroxycamphor,

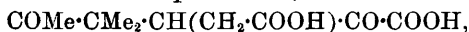
$\text{CH} < \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CH}_2-\text{C}\cdot\text{OH} \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ , is probably formed in traces when the

lactone is heated under reduced pressure, but only the lactone could be obtained by the interaction of isoamidocamphor hydrochloride and sodium nitrite. Béhal's optically active dihydrocampholenolactone, prepared from  $\alpha$ -campholenamide hydriodide, probably contains  $\alpha$ -campholenic acid.

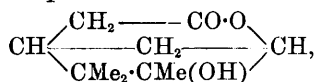
Hydroxydihydrocampholenic acid may be boiled with potassium permanganate without decomposition; at higher temperatures, a part of the acid is oxidised to acetic acid, carbonic anhydride, &c. When  $\alpha$ -campholenic acid is oxidised at low temperatures with the calculated quantity of dilute potassium permanganate solution,  $\alpha$ -anti-

dihydroxydihydrocampholenic acid,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH} < \begin{smallmatrix} \text{CH}_2-\text{CH}\cdot\text{OH} \\ \text{CMe}_2\cdot\text{CMe}\cdot\text{OH} \end{smallmatrix}$

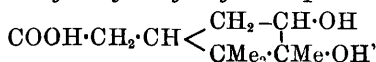
(m. p.  $144^\circ$ ), and *pinonic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH} < \begin{smallmatrix} \text{CH}_2-\text{CO} \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ , are formed. The former is dextrogyrate, and readily yields a hydroxylactone; when oxidised with chromic acid, it gives isoketocamphoric acid (this vol., i, 478), and when cautiously treated with nitric acid is converted into *isodiketocamphoric acid*,



the constitution of which has not yet been absolutely proved. Dihydrocampholenolactone and  $\alpha$ - and  $\beta$ -campholenic acids, when carefully oxidised with chromic acid, in presence of sulphuric acid, yield *hydroxydihydrocampholenolactone*,



melting at  $144^\circ$ .  $\alpha$ -*Syndihydroxydihydrocampholenic acid*,

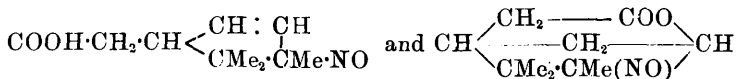


melts at  $91^{\circ}$ , and readily regenerates the lactone, from which it is formed by the action of alkalis. When further oxidised with chromic acid, both hydroxydihydrocampholenolactone and dihydrocampholenolactone yield isoketocamphoric acid, isocamphoronic acid, and terebic acid. It is the study of these reactions that has led the author to revise his previous views on the position of the ethylene linking in the  $\alpha$ - and  $\beta$ -campholene derivatives (see above).  $\beta$ -Campholenic acid, when oxidised with dilute solution of potassium permanganate, yields  $\beta$ -dihydroxydihydrocampholenic acid, which is optically inactive, and melts at  $146^{\circ}$ , and an acid which probably has the formula  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}<\begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ ; it boils  $40-50^{\circ}$  lower than pinonic acid, with which it is isomeric.  $\beta$ -Dihydroxydihydrocampholenic acid, when oxidised with chromic acid, is converted into oxalic acid, and *acetyldimethylbutyric acid*,



which is crystalline, melts at  $48-49^{\circ}$ , and by the action of alkaline bromine solution yields dimethylglutaric acid (m. p.  $85^{\circ}$ ); this, when oxidised with nitric acid, gives unsymmetrical dimethylsuccinic acid.

Béhal and Blaise's recent investigation of the nitrosocampholene derivatives (*Compt. rend.*, **121**, 258) is discussed. According to the author's view, nitrosocampholenic acid (m. p.  $134.5^{\circ}$ ) and nitrosodihydrocampholenolactone have the formulæ



respectively; the ketonic acid (m. p.  $126^{\circ}$ ) is probably either stereoisomeric with pinonic acid, or formed from a  $\gamma$ -lactone into which a portion of the original  $\delta$ -derivative may have been converted. In support of this, it is stated that dihydrocampholenolactone (b. p.  $260^{\circ}$ ), which is certainly a  $\delta$ -compound, yields an isomeric lactone, which boils at  $230-240^{\circ}$ , and is probably a  $\gamma$ -compound; both give the same acid when hydrolysed. The preceding results are fully discussed, and shown to be in complete agreement with the formulæ for camphor, camphoric acid, and the campholenic acids given above, and in the previous communication. The production of campholene from  $\beta$ -campholenic acid and sodium hydroxide is probably preceded by the formation of a hydroxydihydrocampholenic acid,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})<\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ , which

should yield one or other of the hydrocarbons,  $\text{CMe}<\begin{smallmatrix} \text{CH}-\text{CH}_2 \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ ,  $\text{CH}_2\cdot\text{C}<\begin{smallmatrix} \text{CH}_2-\text{CH} \\ \text{CMe}_2\cdot\text{CHMe} \end{smallmatrix}$ . This subject is under investigation. Béhal

has objected to the author's camphor formula on the ground of its inadequacy to explain the production of 1:2:4-trimethylbenzene from campholic acid; as stated in the previous communication, the

conversion of terpenes into benzene derivatives is extremely complex and preceded by the formation of intermediate compounds, which are usually unstable. The subject will be dealt with more fully subsequently.

J. B. T.

**Oxidation and Nitration of Benzylidenecamphor and Benzylcamphor.** By ALBIN HALLER (*Compt. rend.*, 1895, **121**, 35—38).—When a solution of benzylidenecamphor in glacial acetic acid is heated at 100° with fuming nitric acid, it yields a compound,  $C_{17}H_{18}N_2O_5$ , which crystallises in white plates melting at 183°, only slightly soluble in hot alcohol, and soluble in boiling benzene. It is not affected by sodium carbonate solution, and when reduced with tin and hydrochloric acid, it yields the original benzylidenecamphor. It seems to be analogous to the compound obtained by Guthrie from amylene (*Annalen*, **116**, 284, and **119**, 84), or to those obtained by Gabriel from benzylidenephthalide (*Abstr.*, 1885, 902), and probably has the constitution  $C_8H_{14} < \begin{smallmatrix} C(NO_2) \\ O \end{smallmatrix} \cdot CHPh \cdot NO_2$ . This view is sup-

ported by the fact that the same compound is formed when a solution of benzylidenecamphor in glacial acetic acid is gently heated with amyl nitrite and fuming nitric acid.

The prolonged action of hot nitric acid on benzylidenecamphor yields a mixture of camphoric and paranitrobenzoic acids. When oxidised with potassium permanganate, it yields camphoric and benzoic acids.

Benzylcamphor does not yield a nitro-derivative when heated with fuming nitric acid in presence of glacial acetic acid, but prolonged action of hot nitric acid converts it into camphoric and paranitrobenzoic acids, with small quantities of other acids. When oxidised with potassium permanganate, it yields camphoric and benzoic acids.

C. H. B.

**Oxidation of Camphoric acid.** By FRIEDRICH MAHLA and FERDINAND TIEMANN (*Ber.*, 1895, **28**, 2151—2165; compare this vol., i, 426).—The authors mention the work of Wreden (*Annalen*, **163**, 133), Roser (*Abstr.*, 1886, 249), Balbiano (*Abstr.*, 1894, i, 614), Hlasiwetz and Grabowski (*Annalen*, **145**, 212), Kachler (*Abstr.*, 1874, 154), Koenigs (*Abstr.*, 1894, i, 46), and Bredt (*Abstr.*, 1894, i, 141 and 613). It is shown that when *d*-camphoric acid is fused with  $7\frac{1}{2}$  times its weight of potassium hydroxide for 20—40 minutes at a temperature above 400°, the main products are acetic, isobutyric, pimelic (isopropylsuccinic), *d*-cis- and *d*-cistrans-camphoric acids. The authors have succeeded in separating each of these acids, and consider that the hydroxycamphoric acid of Hlasiwetz and Grabowski is merely a mixture of the pimelic and the cis- and cistrans-camphoric acids.

Experiments have been made by treating, with chromic acid mixture, mixtures of propionic and hydroxyisobutyric acids, and of lactic and isobutyric acids, as well as mixtures of their ethereal salts, in order to determine whether trimethylsuccinic acid could be synthesised under such conditions. As their experiments gave negative results, the authors conclude that the trimethylsuccinic acid, obtained by Bredt on oxidising camphoric acid with chromic acid mixture, is a

simple oxidation product of the camphoric acid molecule, and is not the result of a condensation of several simpler oxidation products. They therefore agree with Bredt that the molecules of camphoronic acid, camphoric acid and camphor must contain the grouping  $C \cdot CMe_2 \cdot CHMe \cdot C$ .

The authors also confirm Balbiano's observations on the oxidation of camphoric acid with potassium permanganate (Abstr., 1894, i, 614, and this vol., i, 552). They regard the acid,  $C_8H_{12}O_5$ , which melts at  $120^\circ$ , as a ketonic dicarboxylic acid of the constitution



and not as a hydroxydicarboxylic acid. It yields an *oxime* and a *bromophenylhydrazone*, the latter melting at  $161-162^\circ$ . When heated at  $170-220^\circ$ , the acid loses water and carbonic oxide, and is converted into trimethylsuccinic anhydride; when reduced with hydriodic acid and phosphorous, it yields the acids  $C_8H_{12}O_4$  and  $C_8H_{14}O_4$ , which the authors represent as  $CHMe < \begin{smallmatrix} CMe_2 \\ COO \end{smallmatrix} > CH \cdot COOH$  and  $COOH \cdot CHMe \cdot CMe_2 \cdot CH_2 \cdot COOH$  respectively.

The acid  $C_8H_{14}O_4$ , when further oxidised, yields unsymmetrical dimethylsuccinic acid.

The acetyl,  $CHMe < \begin{smallmatrix} CMe_2 \\ COO \end{smallmatrix} > C(OAc) \cdot COOH$ , and benzoyl derivatives of the acid melting at  $120^\circ$ , have been previously described by Balbiano.

Camphoronic acid is represented as  $COOH \cdot CHMe \cdot CMe_2 \cdot CH(COOH)_2$ , and the authors think that this formula readily accounts for the decomposition of the acid into carbon, carbonic anhydride, trimethylsuccinic acid, and isobutyric acid (compare Bredt, *loc. cit.*).

It is thought that all these facts point to the formulæ recently suggested by Tiemann (this vol., i, 428) for camphor and camphoric acid. Corresponding formulæ for camphanic acid, campholactone, and lauronolic acid are also given. J. J. S.

**Action of Phenylisocyanate on Campholic, Camphocarboxylic, and Phthalic acids.** By ALBIN HALLER (*Compt. rend.*, 1895, 120, 1326-1329).—Campholic acid, when heated with phenylisocyanate at a temperature not exceeding  $100^\circ$ , yields campholic anhydride identical with that obtained by Guerbet by the action of acetic anhydride, but at  $150-160^\circ$  the products are (together with carbonic anhydride) aniline and campholanilide, which melts at  $90-91^\circ$ . Attempts to obtain from campholic acid a phenylurethane analogous to that of benzoïn were unsuccessful. It follows that, in its reactions with phenylisocyanate, campholic acid resembles monocarboxylic acids such as benzoic and toluic acids.

Camphocarboxylic acid, when heated with phenylisocyanate at  $150-170^\circ$ , yields the dianilide,  $C_8H_{14}(CO \cdot NHPh)_2$ , which crystallises from chloroform in white needles melting at  $222-223^\circ$ , and from boiling alcohol in elongated, bevelled lamellæ; it is only slightly soluble in cold alcohol, and insoluble in light petroleum. When heated with concentrated alcoholic potash, the dianilide yields

anilidocamphocarboxylic acid,  $\text{NHPh}\cdot\text{CO}\cdot\text{C}_8\text{H}_{14}\cdot\text{CH}_2\cdot\text{COOH}$ , melting at  $203^\circ$ .

Isophthalic acid heated with phenylic isocyanate at  $150$ — $160^\circ$  yields isophthalic dianilide, which crystallises from acetic acid in white needles melting at about  $250^\circ$ , but is insoluble in most other solvents. Terephthalic acid does not react with the isocyanate even at  $210^\circ$ .

C. H. B.

**Vesicating Constituent of Croton Oil.** By WYNDHAM R. DUNSTAN and LUCY E. BOOLE (*Proc. Roy. Soc.*, 1895, **58**, 238—240).—The authors have examined the vesicating preparation known as crotonoleic acid prepared from croton oil by the method directed by Kobert and Hirscheidt. The lead salt was submitted to a process of fractional precipitation by adding successive quantities of water to its solution in alcohol; by this means crotonoleic acid was proved to be a mixture of inactive oily acids, the lead salts of which are precipitated first, and the true vesicating constituent; the latter, or its lead salt, is principally contained in the last fractions, and represents only a small proportion of the original material.

On saponifying that part of croton oil which is soluble in strong alcohol with a mixture of lead oxide and water and fractionating an alcoholic solution of the lead salts with water, the later fractions, which possessed the greatest vesicating power, furnished a resinous substance having extraordinary power as a vesicant. The authors propose to call it "*croton-resin*." It has the composition  $\text{C}_{13}\text{H}_{18}\text{O}_4$ , cannot be obtained crystalline, and does not yield any crystalline derivatives. It is a hard, pale yellow, brittle resin, nearly insoluble in water, light petroleum, and benzene, but easily soluble in alcohol, ether, and chloroform; when heated, it gradually softens, and is liquid at  $90^\circ$ . It has neither basic nor acid properties, and can be boiled with a mixture of lead oxide and water without any appreciable decomposition. It is gradually decomposed by boiling with aqueous potash and soda, and loses its vesicating power, several acids being formed, some of which are members of the acetic series. When oxidised with nitric acid, a mixture of acids is obtained. Since it is not saponified by lead oxide and water, and as no glycerol could be detected among the products of its decomposition by alkalis, it is not a glyceride, and as it does not react with hydroxylamine or phenylhydrazine or sodium hydrogen sulphite, it is probably neither a ketone nor an aldehyde. The authors hold the view that the constitution is that of a lactone or anhydride of complicated structure.

E. C. R.

**Poisonous Constituents of "*Enanthe crocata*" and of "*Cicuta virosa*."** By JULIUS POHL (*Chem. Centr.*, 1894, ii, 793—794; from *Arch. exp. Pathol. Pharm.*, 1894, **34**, 258—267).—The poisonous principle of *Enanthe crocata* resides mainly in the rhizome. The chief symptom is shocks of clonic cramp, which finally cause general exhaustion and death from stoppage of respiration. *Enanthotoxin*,  $\text{C}_{17}\text{H}_{22}\text{O}_5$  or  $\text{C}_{33}\text{H}_{42}\text{O}_{10}$ , may be extracted from the root by alcohol; it is a dark brown, resinous substance with a peculiar odour. A few

milligrams exhibited to a frog produced cramp closely resembling that caused by picrotoxin, and in the course of half to one hour proved fatal.

*Cicutoxin* is similarly extracted from *Cicuta virosa*; it is somewhat richer in carbon than cœnanthotoxin is, from which it also differs in the greater ease with which it dissolves in alkali, and the difficulty which attends attempts to solidify it by desiccation.

Whether these two substances are really different compounds or differ merely from the presence of impurities remains undecided.

A. G. B.

**Opening of the Thiophen Ring by Piperidine.** By ALBERT TÖHL (*Ber.*, 1895, **28**, 2217—2220).—In attempting to prepare amidothiophen by the action of secondary bases on haloïd derivatives of thiophen, it was found that whilst the influence of a very high temperature is necessary in the case of diethylamine and bromothiophen, the latter is decomposed by piperidine at 240°, yielding a basic product which does not contain sulphur. This *base*, which probably has the constitution  $C_5NH_{10} \cdot CH:C:C:CH \cdot C_5NH_{10}$ , is prepared by heating iodothiophen (12 grams) with piperidine (10.5 grams) for six hours at 200° in a sealed tube; it is a viscous oil, which gradually becomes darker and less mobile on exposure to air. When reduced by adding sodium to the solution in absolute alcohol, it yields *tetramethylenedipiperidide*,  $C_5NH_{10} \cdot [CH_2]_4 \cdot C_5NH_{10}$ , a colourless oil which has the odour of coniine, and boils at 290—300° (uncorr.); the *platinochloride* melts and decomposes at 220°.

*Trimethylenedipiperidide*,  $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$ , is prepared by adding small quantities of trimethylenic bromide to a boiling solution of piperidine in benzene; it boils at 274—275° (uncorr.), and closely resembles the tetramethylene derivative. The *platinochloride* melts and decomposes above 240°, the *hydrochloride* is hygroscopic, and the *aurochloride* melts at 188—190°.

M. O. F.

**Disubstituted Amidacetones.** By RICH. STOERMER and O. DZIMSKI (*Ber.*, 1895, **28**, 2220—2227; compare this vol., i, 479).—When piperidylacetone (*loc. cit.*) is reduced, piperidine and isopropyl alcohol are formed.

*Piperidylhydroxyisobutyric acid*,  $\begin{matrix} C_5NH_{10} \cdot CH_2 \\ | \\ O \text{ — — — } CO \end{matrix} > CMe \cdot OH$ , is obtained

by adding anhydrous hydrogen cyanide to well-cooled piperidylacetone, and allowing the mixture to remain for 24 hours at the ordinary temperature; hydrolysis is effected by gently heating the liquid with concentrated hydrochloric acid, and it is then filtered, boiled with caustic potash, neutralised, evaporated, and the residue extracted with absolute alcohol. The substance forms white, lustrous crystals, and melts at 234°; it dissolves readily in water, but only sparingly in cold alcohol, and is insoluble in ether and chloroform. The *copper* derivative,  $C_5H_6NO_3 \cdot CuOH$ , is hygroscopic, dissolving in water and alcohol with great readiness, but it is insoluble in ether and benzene; the solution is deep blue, and becomes colourless when heated with a few drops of hydrochloric acid. The alkali derivatives were obtained in the syrupy condition, and attempts to prepare alkyl

salts were unsuccessful. The *amide*,  $C_5NH_{10} \cdot CH_2 \cdot CMe(OH) \cdot CONH_2$ , is formed in preparing the acid when the hydrolysis, by means of hydrochloric acid, proceeds very slowly; it crystallises from hot water in long, white needles, and melts at  $153^\circ$ . The *platinochloride* of the amide forms large crystals, and melts at  $198^\circ$ ; the *aurochloride* is crystalline, and melts at  $145^\circ$ .

*Dimethylamidoacetone*,  $NMe_2 \cdot CH_2 \cdot COMe$ , is prepared by adding chloracetone to an aqueous, 30 per cent. solution of dimethylamine; it is a colourless oil, miscible in every proportion with water, alcohol, and ether, and becoming brown on exposure to air. It boils at  $123^\circ$ . The *hydrochloride* is crystalline and very hygroscopic, and the *platinochloride*, which forms beautiful crystals, melts and decomposes at  $176^\circ$ ; the *aurochloride* and *methiodide* melt at  $145$ — $146^\circ$  and  $168^\circ$  respectively. The *oxime* crystallises from benzene in needles, and melts at  $99^\circ$ ; when the vapour is passed through a glowing tube an oily base is produced, probably a derivative of dihydroglyoxaline. The *phenylhydrazone* is an oil.

*Diethylamidoacetone*,  $NEt_2 \cdot CH_2 \cdot COMe$ , is a colourless oil which boils at  $64^\circ$  under a pressure of 16 mm., and at  $155$ — $156^\circ$  under atmospheric pressure; it rapidly becomes brown on exposure to air, and is miscible with water, alcohol, and ether. The *hydrochloride* is less hygroscopic than the salt of the foregoing derivative; the *platinochloride* is crystalline, and melts at  $176^\circ$ ; whilst the *aurochloride* is an oil, and the *methiodide* is hygroscopic. The *oxime* crystallises in flat prisms, melts at  $49^\circ$ , and forms a crystalline *platinochloride*; the *phenylhydrazone* is an oil.

Dimethylamidohydroxyisobutyric and diethylamidohydroxyisobutyric acids have been obtained as syrups, the aqueous solutions dissolving copper carbonate with development of a deep blue colour.

M. O. F.

***n*-Phosphines and *n*-Phosphonium Derivatives.** By C. A. AUGUST MICHAELIS and K. LUXEMBOURG (*Ber.*, 1895, **28**, 2205—2211; compare this vol., i, 430).—*Tripiperidine-n-phosphine*,  $(C_5H_{10}N)_3P$ , is prepared by the action of piperidine (20 grams) on phosphorus trichloride (5.4 grams) in anhydrous ethereal solution at  $0^\circ$ ; it is colourless, crystalline, melts at  $37$ — $38^\circ$ , is slowly decomposed by water or alcohol, and more rapidly by acids; if the acid is highly diluted and the solution cooled, a portion of the base is reprecipitated by alkali, but most of it is resolved into piperidine and phosphorus acid, thus proving that the nitrogen is directly linked to phosphorus.

*Tripiperidinemethyl-n-phosphonium hydroxide*,  $(C_5H_{10}N)_3PMe \cdot OH$ , prepared from the iodide, is crystalline, strongly alkaline, and absorbs carbonic anhydride from the air. The *chloride* and *bromide* are colourless and readily soluble. The *platinochloride* is at first white, but is deposited from alcohol in large, red crystals melting at  $175^\circ$ . The *iodide* crystallises in thick, colourless, cubical crystals melting at  $251$ — $255^\circ$ . The mother liquor deposits a second crystalline compound which is richer in iodine, and is probably  $(C_5H_{10}N)_3P_3MeI$ . Attempts to prepare methylphosphinic acid from the iodide or hydroxide were unsuccessful.

*Tripiperidineethyl-n-phosphinium iodide* resembles the methyl com-



pound, and melts at 178—179°. The *isobutyl* and the *benzyl* compounds are crystalline; the former melts at 172°, the latter is hygroscopic. The *sulphide*,  $(C_8H_{10}N)_3PS$ , is prepared by heating the phosphine and sulphur alone, or in presence of benzene; it crystallises from alcohol in colourless, lustrous plates, melts at 120°, dissolves in concentrated hydrochloric acid, is reprecipitated on dilution, and is also formed by the interaction of piperidine and phosphorus thiochloride.

J. B. T.

**Stereoisomeric Copellidines.** By LUDWIG LEVY and RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 2270—2273; compare Dürkopf, *Annalen*, **247**, 90).—The authors have prepared copellidine by the reduction of aldehydecollidine by Ladenburg's method, and find that a considerable quantity of an *isocopellidine* is formed at the same time. The new base yields a crystalline *hydrochloride* which is very deliquescent, and which is much more readily soluble in acetone than the copellidine hydrochloride. The *hydrobromide* melts at 108—114° and the *aurochloride* at 75—85°. The base itself boils at 160—165°.

Both copellidines may be separated into their optically active isomerides by crystallisation of the tartrates.

The *lævo*-copellidine tartrate is more soluble than the *dextro*-compound, whereas the *dextro*-isocopellidine tartrate is more soluble than the *lævo*-salt.

J. J. S.

**Action of Hydrogen Peroxide on Copellidine.** By LUDWIG LEVY (*Ber.*, 1895, **28**, 2273—2274).—When an acetone solution of copellidine is allowed to stand with a 10 per cent. solution of hydrogen peroxide for about 10 days, it is converted into *ε-amido-ε-methyl-α-ethylvaleraldehyde*,  $COH\cdot CHEt\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$ , which distils under a pressure of 10 mm. at 111—113°, has a specific gravity of 0.9367 at 21°, and possesses characteristic reducing properties.

When warmed with zinc and hydrochloric acid, it yields copellidine, and when treated with sodium hydrogen sulphite solution gives *copellidinesulphonic acid* which melts at 139°.

J. J. S.

**Isoquinoline Derivatives.** By ADOLPH CLAUS and CARL GUTZEIT (*J. pr. Chem.*, 1895, [2], **52**, 9—22).—*Hydroxyisoquinoline*,  $C_9NH_7\cdot OH$  [ $OH = 1$  or  $4$ ], is best prepared from the corresponding amido-compound by heating it with fuming hydrochloric acid at 275—280° for six hours; it forms yellowish crystals melting at 130°, and is identical with the substance obtained by fusing the less soluble isoquinoline-sulphonic acid (following abstract) with caustic potash. The *hydrochloride*, *platinochloride*, with  $2H_2O$ , and *sulphate* melt, or decompose, at 207°, 300°, and 279—280° respectively; the additive compounds with *methylic iodide*, *ethylic bromide* and *iodide*, and *benzylic chloride*, the three last containing each  $2H_2O$ , melt at 239°, 78° (200°), 80° (275°), and 117° (202°) respectively, the numbers in brackets referring to the anhydrous substances; by adding silver chloride, sulphate, and nitrate to the methiodide compound there were obtained a corresponding *chloride*, with  $1\frac{1}{2}H_2O$ , *sulphate*, and *nitrate* melting, or decomposing, when anhydrous, at 259°, 270—280°, and 172° respectively; with potassium dichromate, any of the methylic compounds

yield a brown *dichromate*; all the other compounds crystallise in yellow needles. By treating the methiodide, ethiodide, and benzylochloride with moist silver oxide, the corresponding quaternary ammonium hydroxide compounds are obtained; these crystallise with 1, 2, and  $2\text{H}_2\text{O}$  respectively, are respectively yellow, yellow, and red in colour, and decompose at  $130^\circ$ ,  $160^\circ$ , and  $110^\circ$ .

By boiling the hydroxyisoquinoline with ethylic iodide and alcoholic potash, *ethoxyisoquinoline* is obtained; this, in the impure state, formed a thick, brown oil; its *ethiodide* melts at  $170^\circ$ , and when heated with silver chloride, yields the corresponding *chloride*, which melts at  $63^\circ$ . *Amidoisoquinoline* yields a *methiodide* which melts at  $228^\circ$ ; the *chloride* melts at  $288^\circ$ , the *nitrate* at  $203^\circ$ , and the sulphate at  $230^\circ$ . The *ethbromide* melts at  $257^\circ$ , the *ethiodide* at  $216^\circ$ , and the *benzylochloride*, with  $2\text{H}_2\text{O}$ , at  $88^\circ$  ( $218^\circ$ ). These all crystallise in yellow needles. When the methiodide, either of hydroxy- or amido-isoquinoline is treated with silver oxide, a quaternary ammonium hydroxide, insoluble in ether, is formed; if, however, caustic potash be used, instead of silver oxide, a substance is obtained which is soluble in ether, but which must yet be a quaternary base, since it yields the same hydrochloride as does the base obtained with silver oxide. This behaviour is characteristic of the derivatives of quinoline, not of those of isoquinoline. C. F. B.

**Isoquinolinesulphonic acids.** By ADOLPH CLAUS and ALEX. SEELEMANN (*J. pr. Chem.*, 1895, [2], 52, 1—8).—When isoquinoline is heated with fuming sulphuric acid containing 50—60 per cent. of anhydride, two sulphonic acids are formed; at  $115^\circ$  the less soluble acid is formed in larger amount, at  $250$ — $260^\circ$  the more soluble one. *Isoquinolinesulphonic acid*,  $\text{C}_9\text{NH}_7\text{SO}_3\text{H} + \text{H}_2\text{O}$  [ $\text{SO}_3\text{H} = 1$  or  $4$ , formerly wrongly regarded as  $3$  or  $2$ ], is the less soluble acid; it crystallises in yellowish-green, monoclinic prisms [ $a : b : c = 0.6560 : 1 : 0.4931$ ;  $\beta = 83^\circ 29'$ ] the *potassium salt*, with  $\text{H}_2\text{O}$ , crystallises in yellow rhombic prisms [ $a : b : c = 0.3063 : 1 : 0.385$ ]; the *sodium*, *ammonium*, *calcium*, and *barium salts* form colourless crystals containing respectively  $3\text{H}_2\text{O}$ ,  $1\text{H}_2\text{O}$ ,  $2\text{H}_2\text{O}$ , and  $9\text{H}_2\text{O}$ . The more soluble acid [ $\text{SO}_3\text{H}$  probably =  $3$  or  $2$ ] was obtained, with  $\text{H}_2\text{O}$ , as a crystalline powder; its *barium salt*, with  $6\text{H}_2\text{O}$ , as a greyish-brown, granular mass. C. F. B.

**Nitromethylisoxazolone.** By MILORAD JOVITSCHITSCH (*Ber.*, 1895, 28, 2093—2101).—The product formed by the action of concentrated nitric acid on oximidomethylisoxazolone has most probably the constitution  $\text{CMe} \begin{smallmatrix} \text{N} \text{---} \text{O} \\ \diagdown \quad \diagup \\ \text{CH}(\text{NO}_2) \cdot \text{CO} \end{smallmatrix}$ , and is, therefore, *nitromethylisoxazolone*. The *sodium salt* is probably derived from the hydrated acid, and has the composition  $\text{C}_4\text{H}_5\text{NaN}_2\text{O}_6 + \text{H}_2\text{O}$ . Nitromethylisoxazolone is completely decomposed by boiling with alkalis, carbonic anhydride, nitrous acid, acetic acid, and hydrogen cyanide being among the products of the reaction. *Nitromethylethylisoxazolone*,  $\text{CMe} \begin{smallmatrix} \text{N} \text{---} \text{O} \\ \diagdown \quad \diagup \\ \text{CEt}(\text{NO}_2) \cdot \text{CO} \end{smallmatrix}$ , obtained by the action of ethylic iodide on the

silver salt, crystallises in long, silky needles, and melts at  $68^{\circ}$ . It is hydrolysed in the normal way by alkalis. The *phenylhydrazine salt* of nitromethylisoxazolone crystallises in yellow needles, and the *aniline salt* is also crystalline. Nitromethylisoxazolone is converted by concentrated aqueous alkalis in the cold into a substance which has the composition of *nitracetoxime*,  $\text{NOH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{NO}_2$ . It is a yellow oil, and yields hydroxylamine when treated with hydrochloric acid. Bromine converts nitromethylisoxazolone, in aqueous solution, into a *dibromo-derivative*,  $\text{C}_3\text{H}_4\text{Br}_2\text{N}_2\text{O}_3$ , which is also formed by the action of bromine on a chloroform solution of nitracetoxime. It crystallises in needles, and melts at  $86^{\circ}$ . When exposed to the air, it loses hydrogen bromide, and is converted into a *monobromo-derivative*,  $\text{C}_3\text{H}_3\text{BrN}_2\text{O}_3$ , which melts at  $62^{\circ}$ . A. H.

**Aliphatic Amidoketones.** By HERMANN KÜNNE (*Ber.*, 1895, 28, 2036—2044; compare *Abstr.*, 1893, i, 734).—*Methyl amidoethyl ketone hydrochloride*,  $\text{COMe}\cdot\text{CHMe}\cdot\text{NH}_2\cdot\text{HCl}$ , is obtained by reducing methyl isonitrosoethyl ketone with stannous chloride and hydrochloric acid; it crystallises in slender, white needles, and melts at  $111^{\circ}$ , previously becoming brown. The salt is hygroscopic, and is readily soluble in alcohol; it reduces Fehling's solution. The *platinochloride* melts at  $191$ — $192^{\circ}$ . The base combines with phenylhydrazine, forming dimethylphenylglyoxalosazone, which is identical with the diacetylosazone described by v. Pechmann. When the hydrochloride is heated on the water bath with potassium thiocyanate, *dimethylimidazolyl mercaptan*,  $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ || \\ \text{CMe}-\text{N} \end{array} \gg \text{C}\cdot\text{SH}$ , is formed; it crystallises from

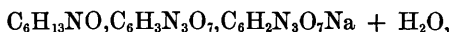
boiling water in pale yellow needles, and blackens at  $270^{\circ}$ . The base has a bitter taste, and in aqueous solution develops a dark red coloration with platinum tetrachloride, and with gold chloride a blood red coloration. Oxidation with ethylic nitrite converts it into *dimethyl-*

*imidazole*,  $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ || \\ \text{CMe}-\text{N} \end{array} \gg \text{CH}$ , which crystallises from ether in yellowish, quadratic plates, and melts at  $117^{\circ}$ ; the *aurochloride* crystallises in yellow prisms, and melts at  $174^{\circ}$ , and the *nitrate* crystallises from alcohol in pale yellow needles, and melts and evolves gas at  $164^{\circ}$ .

*Dimethylimidazolone*,  $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ || \\ \text{CMe}\cdot\text{NH} \end{array} > \text{CO}$ , is formed when the hydrochloride of methyl amidoethyl ketone is heated with potassium cyanate on the water bath; it becomes brown at  $210^{\circ}$ , and begins to sublime at  $280^{\circ}$ . Tetramethylpyrazine is obtained from methyl amidoethyl ketone by successive treatment with potash and mercuric chloride; on distilling off one half of the liquid, and neutralising the distillate, mercuric chloride solution precipitates the mercuriochloride of tetramethylpyrazine.

*Methyl amidobutyl ketone hydrochloride*,  $\text{COMe}\cdot\text{CHPr}\cdot\text{NH}_2\cdot\text{HCl}$ , is obtained by reducing isonitrosobutyl methyl ketone with stannous chloride and hydrochloric acid; it crystallises in slender, white needles, and melts at  $169$ — $170^{\circ}$ . It reduces Fehling's solution when

heated. The *platinochloride* crystallises in orange-yellow, quadratic plates, and melts at 163°; the *sodium picrate*,



becomes anhydrous at 100°, and melts at 118—119°. *Methylpropyl-*

*imidazolyl mercaptan*,  $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ \text{CPr}-\text{N} \end{array} > \text{C}\cdot\text{SH}$ , or  $\begin{array}{c} \text{CPr}\cdot\text{NH} \\ \text{CMe}-\text{N} \end{array} > \text{C}\cdot\text{SH}$ , is ob-

tained by the action of potassium thiocyanate on methyl amidobutyl ketone; it crystallises from dilute alcohol in white needles, and melts at 254—255°. The solution in hydrochloric acid develops a deep red coloration with gold and platinic chlorides. On oxidation, it yields methylpropylimidazole, which was not isolated in the pure state; the *aurochloride* crystallises from water in golden-yellow prisms, sinters at 137°, and melts at 138—139°, and the *picrate* melts at 151°. *Methyl benzenesulphamidobutyl ketone* is obtained by the action of benzenesulphochloride on methyl amidobutyl ketone; it melts at 97·8°.

*Methylpropylimidazolone*,  $\begin{array}{c} \text{CPr}\cdot\text{NH} \\ \text{CMe}\cdot\text{NH} \end{array} > \text{CO}$ , is prepared by heating methyl amidobutyl ketone and potassium cyanate on the water bath; it becomes brown at 235°, and melts and decomposes at 263°. Dimethyldipropylpyrazine is obtained by the successive action of potash and mercuric chloride on methyl amidobutyl ketone; the *aurochloride* melts at 110° and the *picrate* at 95°, sintering at 92—93°.

M. O. F.

**Constitution of *n*-Phenylpyrazolone.** By LUDWIG CLAISEN (*J. pr. Chem.*, 1895, [2], 52, 78—80).—A reply to v. Rothenburg (this vol., i, 570).

C. F. B.

**Syntheses in the Pyrazole Series.** By R. v. ROTHENBURG (*J. pr. Chem.*, 1895, [2], 52, 23—44 and 45—48).—3-*Phenylpyrazolone*,  $\text{C}_9\text{H}_5\text{N}_2\text{O}$ , is obtained by the condensation of hydrazine hydrate with ethylic benzoylacetate in alcoholic solution; it melts at 236°; its *sodium*, *calcium*, and *silver* salts were prepared, and its *hydrochloride*, which melts at 196°. When it is heated with benzaldehyde, 2 atoms of hydrogen are replaced by the group  $\text{CHPh}$ , and 4-*benzylidene-3-phenylpyrazolone*,  $\begin{array}{c} \text{N}\cdot\text{CPh} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}\cdot\text{CHPh}$ , is formed; this is a red, crystalline substance melting above 250°. When 3-phenylpyrazolone is suspended in water and treated with aqueous nitrous anhydride, a yellow or red *isonitroso-derivative*,  $\text{C}_9\text{H}_5\text{N}_3\text{O}_2$ , melting at 188° or 184°, is formed; the red *silver salt* of this decomposes at 242°. From this salt, *ethyl*, *acetyl*, and *benzoyl* derivatives may be prepared by replacement of the silver atom; they are respectively red, yellow, and purple, and melt at 153°, 82°, and 142°. Alkaline reducing agents convert the isonitroso-compound back again into 3-phenylpyrazolone; acid reducing agents, such as zinc dust and acetic acid, reduce it to 4-*amido-3-phenylpyrazolone*; this was not isolated, but its yellow *benzylidene-amido-derivative*, melting at 152°, was prepared by the action of benzaldehyde, and it was oxidised by ferric chloride to a purple 3-*phenylpyrazolonerubazonic acid*,  $\text{C}_{18}\text{H}_{13}\text{N}_6\text{O}_2$ , decomposing at 124°. The action

of the calculated quantity of acetic anhydride on 3-phenylpyrazolone in acetic acid solution converts it into a 1-acetyl derivative, which melts at 122° and yields a *silver salt*. Excess of acetic anhydride brings about the formation of a diacetyl compound, which must, however, be a derivative of isopyrazolone, 1 : 2-diacetyl-3-phenylisopyrazolone,  $\text{NAc} \cdot \text{CPh} \begin{smallmatrix} | \\ \text{NAc}-\text{CO} \end{smallmatrix} \text{>CO}$ ; this melts at 86°, and forms no salts. 3-Phenylpyrazolone also yields a yellow *dibromo-derivative*, melting at 189°, and a purple 4-azobenzene derivative, which melts at 207.5° and yields a yellow 1-acetyl derivative, melting at 199°, and a 1 : 2-benzylidene derivative, melting at 131°. 3-Phenylpyrazolone, when heated with methylic iodide and methylic alcohol, forms a 1-methyl derivative melting at 207°; when treated in alkaline methyl alcoholic solution with methylic iodide, it yields a small quantity of a 4-methyl derivative, melting at 138°. 3-Phenylpyrazolone cannot be reduced in any simple manner; excess of permanganate oxidises it to benzoic acid, but it is converted by the amount of permanganate theoretically necessary to oxidise it to benzoylformic acid into yellowish *phenylimidoacetic acid*,  $\text{NH} \cdot \text{CPh} \cdot \text{COOH}$ , which melts at 59°, and, when treated with phenylhydrazine acetate, yields the yellow *phenylhydrazone of benzoylformic acid*,  $\text{N}_2\text{HPh} \cdot \text{CPh} \cdot \text{COOH}$ , melting at 152°. Acid oxidising agents, such as boiling solution of ferric chloride, convert 3-phenylpyrazolone into 3-phenylpyrazolone blue; the two  $\text{CH}_2$  groups in two molecules being converted into the group  $\text{C} \equiv \text{C}$ , and the two molecules thus joined together.

3-Methylpyrazolone yields a yellow 4-dibromo- and a purple 4-azobenzene derivative; these melt respectively at 182° and 197°. With methylic iodide and methylic alcohol, it yields 1 : 2 : 3-trimethylisopyrazolone; and, when treated with just enough permanganate to oxidise the methyl group to carboxyl, it is oxidised to pyruvic acid, together with a little pyrazolone-3-carboxylic acid.

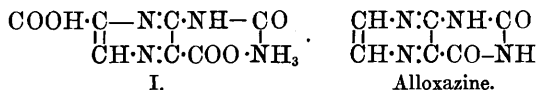
3 : 4-Dimethylpyrazolone is obtained by the action of hydrazine on ethylic methylacetoacetate, and melts at 249°. It yields a reddish-grey 4-benzylidene derivative, the  $\text{CHPh}$  group replacing the two 4-hydrogen atoms in 2 mols. of the pyrazolone; also a 1 : 2-diacetyl (iso), a 4-nitroso (?), and a 4-azobenzene derivative; these melt at 129°, 44°, 214°, and 188° respectively. It is oxidised by the amount of permanganate necessary to convert the two methyl groups into carboxyl to a base melting at 225°, the constitution of which was not ascertained.

3 : 4 : 4-Trimethylpyrazolone is obtained by the action of hydrazine on ethylic dimethylacetoacetate, and melts at 269°. It yields but few derivatives, both hydrogen atoms of the pyrazolone  $\text{CH}_2$  group being now replaced by methyl. It does, however, yield a 1-acetyl derivative, which melts at 168°, and it is oxidised by the amount of permanganate just necessary to convert the three methyl groups into carboxyl, to the same substance as was obtained in the oxidation of dimethylpyrazolone.

Many of the experiments in the second paper have already been described (Abstr., 1894, i, 273, 344, 348, 384).—3-Phenylpyrazole is obtained, together with much of the 5-isomeride, by the action of

hydrazine on benzoylaldehyde in alcoholic solution; it melts at 228°. 3 : 4 : 5-*Trimethylpyrazole* is obtained by the action of hydrazine on methylacetylacetone; it melts at 138—139° and boils at 234—236°, and it is oxidised by alkaline permanganate to *pyrazole-3 : 4 : 5-tricarboxylic acid*, which crystallises with 2H<sub>2</sub>O, yields a crystallised *potassium dihydrogen salt*, and is converted into pyrazole when heated above 230°. 5-*Methylpyrazoline* was obtained by the action of hydrazine on crotonaldehyde in alcoholic solution; it is an oil boiling, with partial decomposition, at about 160°. The rest of the paper is devoted to theoretical considerations. C. F. B.

**Oxidation of Tolualloxazine.** By OTTO KÜHLING (*Ber.*, 1895, 28, 1968—1971).—The acid obtained by the oxidation of tolualloxazine with potassium permanganate (*Abstr.*, 1894, i, 624) loses carbonic anhydride when heated at 190° with dilute hydrochloric acid (6—7 per cent.); the product dissolves in alkalis, and probably has a betaine structure (I),



for it does not yield an acetic derivative, and evolves only traces of ammonia when boiled with strong aqueous alkalis. It melts at 284° with evolution of gas; at 250° it loses water, and the substance formed sublimes at 320°, yielding a yellow sublimate which is *alloxazine* itself. This substance melts above 310°; it has acid properties, and it is very stable towards acids and alkalis; when fused with caustic alkalis, it yields ammonia and hydrogen cyanide together with other products. C. F. B.

**Apoquinine and its Rotatory Power.** By EDUARD LIPPMANN (*Ber.*, 1895, 28, 1971—1972).—The author traverses Hesse's statements (*Ber.*, 1895, 28, 1301). To get pure apoquinine, it is necessary to use dilute hydriodic, in place of hydrochloric, acid, and to precipitate the iodine with silver nitrate; ether then extracts a base which crystallises in colourless prisms containing ether of crystallisation, which is lost only slowly at 110°; the crystals have then become yellow, and have specific rotation  $[\alpha]_D = -217.1^\circ$ .

As to the formation of isomerides of quinine, this is probably one of the first stages of the reaction, but the whole subject is a difficult one. Two bases, melting respectively at 170—171° and 209—211°, have already been obtained. C. F. B.

**Reduction of Cinchonine.** By FR. KONEK V. NORWALL (*Ber.*, 1895, 28, 1843—1844).—The author maintains the accuracy of the results obtained by him in his work on cinchonine (this vol., i, 521), which has been criticised by Hesse (this vol., i, 630). A. H.

**Cinchonidine.** By FERDINAND ROQUES (*Compt. rend.*, 1895, 120, 1170—1173).—Cinchonidine, obtained from the oxalate after the

latter has been carefully purified by repeated recrystallisation, will not crystallise from its ethereal solution in presence of air, but deposits more or less oily, amorphous products, as described by previous observers. If, however, the ethereal solution is dried by means of potassium hydroxide, and evaporated in a current of hydrogen at a comparatively low temperature, the alkaloid separates in crystals. The best results are obtained by evaporating first at about  $25^{\circ}$  or  $30^{\circ}$ , and finally at the ordinary temperature.

Cinchonicine has the composition  $C_{19}H_{22}N_2O$ , and its crystals are long, amber-yellow prisms with curved faces, belonging to the triclinic system. It melts at  $49-50^{\circ}$ , alters rapidly when exposed to air, deliquescing to a syrupy liquid, and dissolves in the ordinary solvents, but crystallises only from ether. Its rotatory power in a 1 per cent. alcoholic solution is  $[\alpha]_D = +48.25^{\circ}$ , and in presence of 2 mols. HCl,  $[\alpha]_D = +28.72^{\circ}$ . The base liberates ammonia from ammonium chloride, and is readily precipitated by picric acid.

The double cinchoninic zinc chloride,  $C_{19}H_{22}N_2O, 2HCl, ZnCl_2 + 2H_2O$ , and the analogous cadmium compound, crystallise in colourless, transparent needles; the methochloride in colourless, anhydrous needles, which melt at  $159^{\circ}$  (corr.), and the methiodide in yellow, anhydrous crystals, which alter somewhat readily; the ethobromide is similar to the methochloride, whilst the ethiodide forms a fine, yellow, anhydrous powder, which alters somewhat readily. The hydrochloride and hydrobromide have not yet been isolated.

The substance described as cinchonicine by W. v. Miller and Rohde (this vol., i, 434), does not seem to be identical with the cinchonicine isolated by the author. C. H. B.

**Alkaloids of Fumariaceæ and Papaveraceæ.** By J. A. BATTANDIER (*Compt. rend.*, 1895, **120**, 1276—1277).—The crude alkaloids from Papaveraceæ, such as *Bocconia*, *Hypecoum*, *Eschscholtzia*, and *Glaucium*, give with sulphuric acid a reaction very similar to that of fumarine. The root of *Bocconia frutescens* contains fumarine identical with that obtained from *Fumaria*; another alkaloid, which the author calls *bocconine*, and which gives a peach-blossom colour with sulphuric acid; traces of a third, which gives reactions similar to those of chelidonine; and a large quantity of chelerythrine.

Fumarine, some time after it has been precipitated, becomes only slightly soluble in water and most organic solvents, even at their boiling points, but is very soluble in chloroform. Its hydrochloride crystallises in heavy, transparent needles. With cold, concentrated sulphuric acid, fumarine gives a deep violet, almost blue, coloration, changing to brownish-black on the addition of potassium dichromate; traces of bocconine seem to modify this coloration.

*Bocconine* is relatively somewhat soluble in water and most neutral solvents, and crystallises in white, nacreous, silky tufts. The hydrochloride crystallises in similar forms. With most reagents, it gives reactions very similar to those of fumarine, but its salts are more soluble, and the colour with sulphuric acid is characteristic.

*Chelerythrine* is present in somewhat high proportions in the bark of *Bocconia*, to which it gives its red colour. When boiled with con-

centrated nitric acid, the deep red solutions of chelerythrine are decolorised, but on adding excess of ammonia, the liquid becomes red. *Eschscholtzia californica* grows readily in Algeria, and the juice of the root is rich in chelerythrine.

*Glaucine*.—The glaucine described by Probst contained small quantities of fumarine; when carefully purified it gives only a very faint, greenish-blue tint with concentrated sulphuric acid. On heating, however, the deep violet compound described by Probst is always obtained. The hydrobromide and hydriodide are the only glaucine salts that crystallise readily; the latter is less soluble in water than the former.

C. H. B.

**Yellow Colouring Matter of the Urine.** By ARCHIBALD E. GARROD (*Proc. Roy. Soc.*, 1894, **55**, 394—407).—For previous work compare Thudichum (*Brit. Med. Journ.*, 1864, **2**, 509) and Schunck (*Proc. Roy. Soc.*, 1867, **16**, 85). Uroblin, hæmatoporphyrin, and, occasionally, uroerythrin occur as pigments in urine, but the quantity of each is too small to account for the yellow coloration. The author has succeeded by the following process in extracting a new colouring matter. The concentrated urine is saturated with pure ammonium sulphate, filtered, and to the filtrate absolute alcohol is added; this causes it to separate into two layers, the upper alcoholic layer containing the pigment. The latter, purified by a tedious process, the details of which are given in the paper, is ultimately obtained as a brown, amorphous mass. The substance thus obtained is not quite pure, but usually contains a little urea mixed with it. It is very hygroscopic, and readily soluble in water and in rectified spirit, but less so in absolute alcohol, and quite insoluble in ether, benzene, or chloroform. The solution shows no absorption bands, does not fluoresce when zinc chloride and ammonia are added, and is readily decolorised by nascent hydrogen. The solution, when treated with nitric acid, gave the xanthoproteic reaction. Precipitates containing the bulk of the pigment were obtained with lead acetate, mercuric acetate, silver nitrate, phosphotungstic acid, and phosphomolybdic acid, but not with mercurous acetate. When a colourless solution of uric acid is added to a solution of the pigment and allowed to crystallise, yellow or brown crystals are obtained which are indistinguishable from those of natural urinary sediments. The author thinks that the products obtained by Thudichum, Tichborne, and Schunck are probably the same as his, only in a more or less impure state.

J. J. S.

**Reduction of Alkaline Copper Solutions by Proteïds.** By EDMUND DRECHSEL (*Zeit. physiol. Chem.*, 1895, **21**, 68—70).—Krukenberg stated that at the boiling temperature there is in the so-called biuret reaction of proteïds a reduction of the cupric to cuprous oxide, the latter, however, remaining in solution. The present research shows that this reduction also occurs at the ordinary temperature; it is, however, very slow and incomplete. The solutions were kept for a year before they were examined. The substances used were Witte's peptone, and deutero-albumose. This result does



not necessarily mean that these substances contain a carbohydrate radicle, for many substances not carbohydrates reduce Fehling's solution. W. D. H.

**Mode of Combination of Sulphur in Albumin.** By F. SUTER (*Zeit. physiol. Chem.*, 1895, 20, 564—582).—The following substances were tested in order to ascertain to what extent the sulphur which they contain is precipitated when they are heated in alkaline solution with lead acetate. The precipitation from cystine, with or without peptone, and cysteine is incomplete, and proceeds very slowly, only 60 per cent. being obtained after 9·5 hours. Hair and feathers deposit 98·8 and 98 per cent. after 9 and 15 hours respectively; egg albumin and peptone behave in a similar manner; these compounds therefore resemble cystine. The production of a clear filtrate is no criterion of complete precipitation. Under similar conditions the sulphur is completely precipitated from thiocarbamide and allylthiocarbamide. Attempts were made to isolate cystine or cysteine from residues obtained during the preparation of tyrosine, but without success; these substances are not, therefore, direct decomposition products of horn, but they may possibly be formed in traces. The above mother liquor contained  $\alpha$ -thiopropionic acid in rather small quantity; this was recognised by its benzyl derivative which crystallises in colourless prisms, melts at 73°, and is identical with the synthetical compound obtained from benzylic mercaptan and ethylic  $\alpha$ -bromopropionate. A second substance, which has strongly acidic properties, and contains sulphur, was also isolated from the tyrosine mother liquor; it gives a blue coloration with ferric chloride, and a fugitive violet with copper sulphate; it does not yield a benzyl derivative, and is possibly thioglycollic acid (compare following abstract),  $\alpha$ -Thiopropionic acid is not a primary decomposition product of albumin. By the action of hydrogen sulphide on pyruvic acid in aqueous solution, in presence of sodium acetate,  $\alpha$ -thiopropionic acid is formed; pyruvic acid is also not a primary decomposition product of albumin, as it is not present in the tyrosine mother liquor.

J. B. T.

**Sulphur Derivatives of Albumins and their Interrelationship.** By EUGEN BAUMANN (*Zeit. physiol. Chem.*, 1895, 20, 583—585; compare preceding abstract).—The formation of  $\alpha$ -thiopropionic acid from cysteine resembles that of hydroxyparacoumaric acid from tyrosine. It is very probable that the ethylic sulphide, which J. J. Abel found in dog's urine, particularly after a meat diet, is produced by the decomposition of  $\alpha$ -thiopropionic acid. Nencki has shown that methylic mercaptan is formed during the decomposition of albumin, and should Suter's observation of the occurrence of thioglycollic acid be confirmed, these would appear to be related, like ethylic mercaptan and  $\alpha$ -thiopropionic acid. The primary thio-decomposition product of albumin is unknown; possibly it may prove to be a thioaspartic acid,  $\text{NH}_2\text{C}(\text{SH})(\text{COOH})\cdot\text{CH}_2\text{COOH}$ .

J. B. T.

**The Behaviour of Casein in Ammoniacal Magnesium Chloride Solution.** By WACŁAW V. MORACZEWSKI (*Zeit. physiol.*

*Chem.*, 1895, **21**, 71—78).—A solution of casein free from ash (caseinogen), when mixed with ammoniacal magnesia mixture, proceeds, after some days, to deposit sphæroliths; these, by attention to details, described in full in the paper, can be obtained in the form of aggregations of needles. They contain 45 per cent. of ash, and 14.98 per cent. of nitrogen. The nature of this proteid compound of magnesium is, however still uncertain.

Nuclein also yields a crystalline deposit with ammoniacal magnesia mixture. W. D. H.

**Precipitation of Toxalbumins by Nucleic acid.** By M. TICHOMIROFF (*Zeit. physiol. Chem.*, 1895, **21**, 90—96).—Ricin is precipitable by nucleic acid. The precipitate can be redissolved, and, when tested on animals, is found to be still as poisonous as before. The same was found to be true for tetanus poison and diphtheria poison. The addition of nucleic acid to solutions of cholera poison and to cultures of streptococci, *Staphylococcus aureus*, and typhoid bacilli (in all cases freed from the growth of micro-organisms) produced a precipitate, which, however, was not poisonous. From putrefying beef, the precipitate was also not active; but a poisonous precipitate was obtained from putrefying fish. W. D. H.

**Amylase.** By JEAN EFFRONT (*Compt. rend.*, 1895, **120**, 1281—1282).—An infusion of barley prepared at the ordinary temperature, boiled and filtered, greatly increases the diastatic power of malt, and thus resembles aluminum and vanadium salts, asparagine, picric acid, &c. (*Abstr.*, 1893, i, 187). Since, however, in all cases the saccharifying power only is increased, whilst the liquefying power is practically unaffected, and the effect disappears in presence of such quantities of amylase as are required to produce energetic saccharification, the increase in saccharifying power is more apparent than real.

A comparison between the saccharifying and liquefying powers of malts yields better results than the methods of Kjeldahl and Lindner. The substance to be examined is extracted with eight times its weight of water. The saccharifying power is measured by the volume of the solution required to produce in an hour, at 45°, 0.25 to 3 grams of maltose per 100 c.c. of starch paste, the experiment being made with 150 c.c. of a 1 per cent. solution of starch. The liquefying power is expressed by the volume of the solution required to liquefy in 10 minutes, at 80°, 20 c.c. of milk of starch containing 40 parts of starch in 100. The ratio between the saccharifying and liquefying powers in good malt is 100 to 120, but in presence of substances that increase the saccharifying power it may rise to 200—400. The diastase of the crude barley shows a ratio of more than 1000. The saccharifying power being equal, the value of two malts is proportional to the ratios between the saccharifying and liquefying powers. C. H. B.

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# JOURNAL

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## THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART II.

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#### General and Physical Chemistry.

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**Molecular Asymmetry and Rotatory Power of Organic Substances.** By A. PIUTTI (*Gazzetta*, 1894, **24**, ii, 85—97).—The author gives an account of Guye's theory respecting the molecular rotations of organic substances, and shows that the most complete disaccord exists between the experimental and calculated rotations of many derivatives of asparagine. W. J. P.

**Method of Determining Rotatory Dispersion by the Aid of Ray Filters.** By H. LANDOLT (*Ber.*, 1894, **27**, 2872—2887).—To measure the rotatory dispersion of those substances which rotate the plane of polarised light recourse has hitherto been had to the combination of a polarimeter and a spectrometer; this combination, however, besides being too complicated for the chemical laboratory, necessitates a very powerful light. Hence the rotatory dispersion of but few substances has been determined.

The employment of sodium light has numerous disadvantages. Lamps that are constructed to furnish flames of sufficient brilliancy need frequent renewal of the sodium chloride, thereby interrupting observations; if sodium bromide be used as recommended by Fleischl v. Marxow (*Abstr.*, 1890, 549), a stronger light is obtained, but this salt volatilises even more quickly than the chloride, and bromine vapour separates from the flame. The sodium light is not strictly homogeneous, and must be freed from other rays; this is best done by Lippich's method (*Zeit. Instrument-Kunde*, 1892, 340), namely, by allowing the light to pass through two glass troughs containing solutions of potassium dichromate and uranic sulphate respectively.

The author finds that it is possible to obtain fairly homogeneous light by selective absorption of white light in the manner to be described. v. Seherr-Thoss employs for this purpose coloured plates, mostly cut from mineral crystals. The author uses Auer's incandescent lamp as the source of light; ordinary gas and petroleum lamps are unsuitable for the purpose, as the light they emit is too poor in blue rays. Coloured glass is not to be recommended as an absorbing agent, on account of the difficulty of obtaining samples of like quality, and he therefore makes use of standard solutions of pure chemicals, which are contained in cylindrical glass troughs of 4 cm. diameter, divided into two or three compartments at definite intervals according to requirement. Lippich's polarimeter was used; instruments of the Laurent type being unsuited for the purpose.

In the case of Lippich's polarimeter, when sodium light is used, the sensitiveness corresponds with the inclination of the principal planes of the two Glan's prisms at an angle of about  $3^\circ$ . This angle is denoted by the symbol  $\phi$ . When, however, the light employed is not strictly monochromatic, as in the case of that obtained by the aid of ray filters, this angle is increased to about  $5^\circ$  for red, green, and bright blue light, and to about  $10^\circ$  for yellow and dark blue light.

*Red Light.*—This may be obtained by the combination of a trough (20 mm. in length), filled with a solution of 0.05 gram of hexamethylpararosaniline hydrochloride (crystal violet 5BC), dissolved in alcohol and diluted with water to 1 litre, with a second trough (of the same length) filled with a 10 per cent. solution of normal potassium chromate. The light thus obtained, when examined in a spectroscope in which the slit of the collimator tube has a width of 0.25 mm., gives a single red band between wave-lengths  $718\ \mu\mu$  and  $639\ \mu\mu$ .

*Yellow Light.*—A 30 per cent. nickel sulphate solution of 20-mm. length absorbs only the red rays; if the light be now passed first through a 15-mm. length of a 10 per cent. solution of normal potassium chromate, and subsequently through a like thickness of a solution of potassium permanganate containing 0.025 gram of that salt in 100 c.c. of water, the spectrum of the issuing light consists of a narrow, orange-yellow band between  $614\ \mu\mu$  and  $574\ \mu\mu$ . The light so obtained is much less brilliant than that from a strong sodium flame, and the removal of the remaining portion of the red rays from it by further absorption cannot be effected without rendering the light too faint for use. With an angle of rotation higher than  $20^\circ$ , the two halves of the field appear of different colours, that is, red and yellow respectively.

*Green Light.*—Obtained by means of a 20-mm. length of an aqueous solution of copper chloride ( $\text{CuCl}_2 + 2\text{H}_2\text{O}$ ; 60 grams in 100 c.c.), and a similar length of 10 per cent. solution of normal potassium chromate. The broad green band of this light is between  $540\ \mu\mu$  and  $505\ \mu\mu$ .

*Bright Blue Light.*—"Double green SF," which consists of a compound of chloromethylhexamethylpararosaniline hydrochloride (methyl-green) with zinc chloride, is dissolved in water so that a solution containing 0.02 gram of the colouring matter in 100 c.c. is

obtained. A 20-mm. length of this solution in conjunction with a similar length of a 15 per cent. solution of copper sulphate gives light which still contains green rays of wave-lengths between  $526 \mu\mu$  and  $494 \mu\mu$ , and bright blue rays between  $494 \mu\mu$  and  $458 \mu\mu$ .

*Dark Blue Light.*—Obtained by means of 20-mm. lengths of solution of "crystal violet 5BO" (0.005 gram in 100 c.c. of water); and of 15 per cent. copper sulphate solution; the wave-length of this light is between  $478 \mu\mu$  and  $410 \mu\mu$ .

The following table shows the ratio between the values obtained with quartz by the method just described, and those obtained by that of Broch, who used light corresponding with different Fraunhofer lines.

Ray Filter.		Fraunhofer lines.	Ratio.
	$\alpha$ .	$\alpha'$ .	$\alpha'/\alpha$ .
Red ( $r$ ) . . . . .	16.78°	C . . . . .	1.0316 $\alpha_c = \alpha_r$
Yellow ( $y$ ) . . . . .	21.49	D . . . . .	1.0102 $\alpha_y = \alpha_D$
Green ( $g$ ) . . . . .	26.85	E . . . . .	1.0257 $\alpha_g = \alpha_E$
Bright blue ( $bh$ ) . . . . .	32.39	F . . . . .	1.0114 $\alpha_{bh} = \alpha_F$
Dark blue ( $db$ ) . . . . .	39.05	G . . . . .	1.0907 $\alpha_{db} = \alpha_G$

The ratios shown in the last column give therefore the factors by which the values obtained by the ray absorption method are to be multiplied in order to convert them into those corresponding with definite Fraunhofer lines. In the table which follows, the agreement is shown between the calculated and directly observed values for sodium light.

	Observed. $\alpha_y$ .	Calculated. $\alpha_D$ .	Observed. $\alpha$ (sodium).
Quartz plate (2.547 mm.) . . . . .	54.74°	55.29°	55.295°
„ (1.575 mm.) . . . . .	33.85	34.19	34.19
„ (0.519 mm.) . . . . .	11.15	11.26	11.27
Tartaric acid (aqueous solution) . . . . .	7.92	8.00	8.02
Turpentine oil . . . . .	15.77	15.93	15.94
Camphor (alcoholic solution) . . . . .	26.26	26.52	26.70

From the observed rotatory powers calculated for 1 mm. of quartz, the wave-lengths corresponding with the light of the five different colours may be ascertained. From these, the rotatory dispersion of quartz may be calculated by Boltzmann's formula

$\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^4}$ , which, with the constants

$$\alpha = \frac{7.108293}{10^6 \cdot \lambda^2} + \frac{0.1477086}{10^{12} \cdot \lambda^4},$$

gives values agreeing closely with those of Sorot and Sarasin (*Compt. rend.*, 1882, 95, 637). The wave-lengths corresponding with the rotatory powers are as follows.

	Red.	Yellow.	Green.	Bright blue.	Dark blue.
$\alpha$ . . . . .	16.78°	21.49°	26.85°	32.39°	39.05°
$\lambda$ . . . . .	665.9	591.9	553.0	488.5	448.2 $\mu\mu$ .

The rotatory dispersion of saccharose, in aqueous solution, was determined by the new method, the results being in close agreement with those of Seyffart, Stefan, and Arndtsen. In the case of santonin, however, which was examined in chloroform solution, the values obtained for the rotatory dispersion by the new method differ considerably from those of Nasini; this is, however, accounted for by the magnitude of the angle of rotation of santonin solution.

In an appendix to this paper, the author shows that, by making use of a Linneman's oxy-coal gas-burner and a zirconia cylinder, a sufficiently strong light may be obtained to render possible the employment of the following combination. 40 mm. of nickel sulphate solution (22 grams in 100 c.c.), 15 mm. of normal potassium chromate solution (10 grams in 100 c.c.), and 15 mm. of potassium permanganate solution (0.025 gram in 100 c.c.). The light thus obtained gives a narrow, yellow band between  $614\ \mu\mu$  and  $578\ \mu\mu$ , containing a very small residue of red rays. The rotatory powers (when not too high or when the dispersion is not too great) observed with the aid of this light agree closely with those in which sodium light is employed.

A. R. L.

**Dependency of the Electrical Conductivity of Organic Salts on the Temperature.** By A. BARTOLI (*Gazzetta*, 1894, **24**, ii, 156—172).—This paper describes the results of a continuation of the author's investigations of the electrical conductivity of organic substances (Abstr., 1886, 191); he draws the following conclusions from a study of about 60 aliphatic salts. At ordinary temperatures, or at the boiling points, the electrical conductivities of aliphatic alkyl salts of small molecular weight is greater than those of their higher homologues. The electrical conductivity of such salts increases with the temperature, the coefficient of increase of conductivity being greater for salts of high molecular weight than for their lower homologues; the temperature coefficient of the conductivity therefore increases as the viscosity of the salt increases. In the one or two cases in which the conductivity decreases with rise of temperature, the anomalous behaviour can be explained by assuming the presence of a trace of an aliphatic alcohol. The conductivity of a salt may be caused to decrease with rise of temperature by adding from 1 to 20 per cent. of any aliphatic alcohol; the electrical conductivity of a salt still increases as the temperature is raised on adding to it aniline, paraldehyde, a phenol, a ketone, or an acid.

W. J. P.

**Electrolysis of Copper Sulphate.** By A. CHASSY (*Compt. rend.*, 1894, **119**, 271—272).—When a hot solution of copper sulphate is electrolysed, a remarkable violet-red deposit is usually obtained. With platinum electrodes and a current of 0.01 ampère per sq. cm., an almost neutral saturated solution of pure copper sulphate at  $100^{\circ}$  yields a bright-red deposit of microscopic crystals derived from the cube and octahedron. These crystals consist of cuprous oxide. Below  $100^{\circ}$ , the cuprous oxide becomes mixed with crystals of copper, the proportion of which is higher the lower the temperature. A

similar effect is produced by increasing the strength of the current or diluting the solution.

If the positive electrode consists of copper, its loss of weight is always distinctly lower than the gain in weight of the negative electrode. Moreover, if the voltameter containing the hot solution is connected in the same series with a voltameter containing a cold solution, the weight of the deposit in the former is always much greater than would correspond with the oxidation of the copper deposited in the latter.

C. H. B.

**Volume Changes in Elements during Melting.** By M. TOEPLER (*Ann. Phys. Chem.*, 1894, [2], **53**, 343–378).—The volume change during melting was determined for a number of elements, and the constant ( $K_e$ ) expressed in c.c. per gram of the element. In the case of elements whose melting points were sufficiently low, glass dilatometers were employed, a column of paraffin or oil protecting the molten element if necessary. The reading was taken at a number of temperatures in the neighbourhood of the melting point for both liquid and solid states, and the difference of the ordinates of the two curves at this temperature gave the required data. In the case of elements with high melting points, an iron vessel was employed, which was filled with the molten element; this was allowed to solidify, and the volume of the cup-shaped depression formed during solidification was determined by the weight of water required to fill it. In the case of sulphur, which can be easily supercooled, the volume-change is given for a number of temperatures, and the volume changes during the transformation of the different modifications of selenium are recorded and depicted graphically. Numerous curves are given, that of sulphur showing a well-marked maximum value at about  $180^\circ$ . The results obtained are given in the accompanying table.

Element.	$k_e$ .	Per cent.	Element.	$k_e$ .	Per cent.
Sodium .....	0·0264	2·5	Cadmium .....	0·0064	5·2
Aluminium .....	0·019	4·8	Tin.....	0·0039	2·3
Sulphur.....	0·0287	5·5	Antimony.....	0·0022	1·4
Potassium .....	0·030	2·5	Tellurium .....	0·0123	—
Zinc .....	0·010	—	Iodine.....	0·0434	21·1
Selenium.....	0·018	—	Thallium.....	0·0027	3·1
Bromine.....	0·0511	—	Lead .....	0·0034	3·7
Rubidium.....	0·014	—	Bismuth .....	—0·0034	—3·27

The author points out that if the constants are taken as ordinates, and the atomic weights as abscissæ, a curve is obtained closely resembling that of the atomic values, so that  $k_e$  is a periodic function of the atomic weight. It is also closely connected with the coefficient of expansion, but the formula expressing the relationship is left undetermined.

L. M. J.

**The Change in the Specific Heat of Water between  $0^\circ$  and  $+32^\circ$ .** By A. BARTOLI and E. STRACCIATI (*Gazzetta*, 1894, **24**, ii, 145—

152; compare Abstr., 1893, ii, 443).—The authors have determined the specific heat of water at temperatures between  $0^{\circ}$  and  $35^{\circ}$ , by three different methods; the results obtained by the three methods usually agree to one part in 10,000. The specific heat of water  $C$ , referred to the specific heat at  $15^{\circ}$  as unity, is represented between  $0^{\circ}$  and  $35^{\circ}$  by the following equation, temperatures being measured on the hydrogen thermometer.

$$C = 1.00688 - 0.000,556t - 0.000,006,15t^2 + 0.000,001,015t^3 - 0.000,000,013t^4.$$

W. J. P.

**Specific Heat of Water at Constant Volume.** By A. BARTOLI and E. STRACCIATI (*Gazzetta*, 1894, 24, ii, 152—155; compare preceding abstract).—The specific heat of water at constant volume calculated from Thomson's formula, using the author's experimental results, decreases continuously as the temperature rises; the ratio of the specific heat at constant pressure to that at constant volume decreases from  $0^{\circ}$  to  $+4^{\circ}$ , and then increases continuously up to  $35^{\circ}$ , the highest temperature at which determinations were made.

W. J. P.

**The Critical State.** By W. RAMSAY (*Zeit. physikal. Chem.*, 1894, 14, 486—490).—The author contends against the supposition that at the critical temperature the liquid and gas possess distinct individuality, and describes the method he adopts for obtaining pure ether at its critical temperature, complete details being given, as absolute purity is a matter of vital importance. The ether, contained in a ring-shaped tube, is heated by the vapour of pure quinoline in a jacket connected with a reservoir and pump so that the temperature can be accurately altered to a small fraction of a degree. At about  $193.5^{\circ}$  the surface of the ether becomes nebulous, and at this point a slight cooling of the one side of the jacket causes a sinking of the substance at that side, and a corresponding rise on the other, owing to the great expansibility in the neighbourhood of the critical temperature; by further cooling a complete circulation of the ether may be effected. The appearance of streaks, usually taken as a sign of the critical state, is no indication, as the nebulosity, when examined by a polariscope, shows the presence of liquid particles suspended in the gas like a cloud. The critical point can, however, be found from two density observations taken at two neighbouring points, the curve being considered a parabola. The critical point of ether, he hence concludes, is  $194.7^{\circ}$  or  $194.8^{\circ}$ , and he emphasises his opinion that at this temperature the substance is completely homogeneous.

L. M. J.

**Critical Density.** By P. A. GUYE (*Chem. Centr.*, 1894, i, 712—713).—The critical density is, according to van der Waals, equal to 2.667 times the theoretical, but the experiments of Young lead to the value 3.85 for the factor. The author points out that, according to a correction of O. Meyers, the ratio should be 3.77.

L. M. J.

**The Volume Changes attending the Mixture of Liquids, in Relation to Cryoscopic Behaviour.** By E. PATERNÒ and C.



MONTEMARTINI (*Gazzetta*, 1894, **24**, ii, 179--190).—The authors have commenced an investigation of the molecular complexity of liquids, and give the results of some preliminary experiments on the densities of mixtures of benzene with methylic, ethylic, isopropylic, isobutylic, caproic and benzylic alcohols, acetic and isobutyric acids and anethoil.

W. J. P.

**Determination of the Osmotic Pressure of Albuminous Liquids by the Cryoscopic Method.** By H. J. HAMBURGER (*Rec. Trav. Chim.*, 1894, **13**, 67--79).—The author has determined, by the cryoscopic method, the osmotic pressure of several albuminous liquids, such as the blood-serum of the horse and of the ox. The results obtained agree with those arrived at by the plasmolytic method, so that it is possible to substitute for this method that of the reduction of the freezing point when difficulty might be experienced in applying the former.

H. C.

**Lowering of the Freezing Point.** By H. C. JONES (*Ann. Phys. Chem.*, 1894, [2], **53**, 392--395).—The results of the author's determinations of the reduction of the freezing point are not concordant with those of Loomis, and suggestions of possible errors in the author's results were made by Kohlrausch (*Abstr.*, 1894, ii, 228). These, however, do not appear to be the true cause of the differences, and suggestion is made of possible impurity in some of Loomis' compounds. The author's results in the case of phosphoric acid are shown to agree well with those of Arrhenius, whilst the results of Loomis differ by as much as 25 per cent.; the "dissociation," as calculated from the author's numbers, also agrees in most cases with that obtained by Kohlrausch by the conductivity method.

L. M. J.

**Solubility of Mixed Crystals of Pairs of Isomorphous Salts.** By W. MUTHMANN and O. KUNTZE (*Zeit. Kryst. Min.*, 1894, **23**, 368--378).—The authors have examined the equilibrium between solid solutions of several pairs of isomorphous salts and their aqueous solutions. The equilibrium between potassium dihydrogen arsenate, and phosphate at 7° is typical of case 1 of Roozeboom's classification (*Abstr.*, 1892, 265), a case not hitherto met with in practice. The curve connecting the composition of the mixed crystals with that of their solution is only slightly above the straight line making 45° with each co-ordinate, that is to say, the composition of the solution differs but slightly from that of the deposited crystals.

The equilibrium between potassium perchlorate and permanganate and their mixed solutions at 7° is of the same kind as that between the potassium and thallium chlorates and their solution (*Abstr.*, 1892, 266); the same is true of potassium and rubidium permanganates.

W. J. P.

**Relation between the Constitution of Fatty Acids and the Solubility of their Salts.** By A. LIEBEN (*Monatsh.*, 1894, **15**, 404--414).—On comparing the solubilities of the calcium, barium, and silver salts of fatty acids, the author finds there are fixed relations, accord-

ing to definite laws, between the constitution of the acids and the solubility of their salts. In the case of the normal acids, the relation is exceedingly simple, each substitution of a methyl group for hydrogen producing a regular change in the solubility of the salts; but in the case of acids other than normal, the connection, although it undoubtedly exists, is not nearly so simple. G. T. M.

**Polymerisation of Liquid Molecules.** By P. A. GUYE (*Chem. Centr.*, 1894, i, 712).—The researches of Ramsay and Shields indicate polymerisation in liquids in which it had previously appeared probable owing to the deviations from van der Waals' law. Polymerisation is also probably indicated in the following case:—(1) If the curve which expresses the mean between the densities in the liquid and gaseous states is not a straight line; (2) if the heat of vaporisation does not decrease continuously with the temperature, but exhibits a maximum value; (3) if the vapour pressure curve cuts those of other liquids; (4) if, in the expression  $\log \pi - \log p = k \frac{\theta - T}{T}$  (where  $\pi$  and  $\theta$  are the critical pressure and temperature), the constant  $k$  does not possess the normal value 3.06; it should be noticed, however, that a normal value does not necessarily indicate absence of polymerisation. For the determination of physicochemical laws, liquids should be chosen in which the molecular state remains unchanged, as otherwise it is probable that the laws are masked, and appear too complicated. L. M. J.

**Velocity of Reaction between Alkylid Sulphides and Alkylid Iodides.** By G. CARRARA (*Gazzetta*, 1894, 24, ii, 68—75; compare *Abstr.*, 1893, i, 633).—The author has previously shown that it is not improbable that, in the thetines, the four valencies of the sulphur atom are of different values. If this is really so, then the velocity of action between ethylic iodide and methylic sulphide should be different from the velocity of reaction of methylic iodide and methylic ethylic sulphide, although the product is, in both cases, dimethylethylthetine. As has been previously shown (*Abstr.*, 1894, ii, 309, 310), these reactions are of the second order, and the expression  $\frac{x}{t(A-x)}$  is constant and equal to AC.

The value AC in the two cases is fairly constant; in the action between methylic sulphide and ethylic iodide, it is 0.00027 at 0°, and in the action of methylic ethylic sulphide on methylic iodide it has the value 0.01223 at 0°. Similarly, the action between ethylic iodide and methylic ethylic sulphide has the velocity constant 0.00014 at 0° and 0.0562 at 36°; the action between methylic iodide and ethylic sulphide proceeds with the velocity 0.00697 at 0°.

As the author remarks, however, these figures do not afford a decisive proof of the different values of the valencies of sulphur, since it has been repeatedly shown (Menschutkin, *Abstr.*, 1890, 1366) that the velocity of reaction of methylic iodide is greater than that of ethylic iodide, the product of the action being the same in the two cases. W. J. P.

**An Aluminium Air Bath.** By L. MEYER (*Ber.*, 1894, **27**, 2769—2770).—Aluminium may be used with advantage for the construction of the air baths devised by the author, on account of its high conductivity for heat and its permanence in the air. The layer of oxide formed does not scale off. The apparatus has now been constructed with side doors, which are more convenient for many purposes than those opening from the top. A. H.

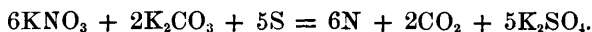
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## Inorganic Chemistry.

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**Ratio of the Atomic Weights of Hydrogen and Oxygen.** By L. MEYER and K. SEUBERT (*Ber.*, 1894, **27**, 2770—2773).—Thomsen has recently (*Abstr.*, 1894, ii, 277) calculated the ratio of the atomic weights of hydrogen and oxygen from the experimental equivalent-ratio of ammonia and hydrogen chloride. The authors point out that in the equation employed by Thomsen,  $H = \frac{rCl - N}{3 - r}$ , in which  $r$  is the experimentally determined ratio of ammonia to hydrogen chloride, there is an uncertainty of 0.01 in the atomic weights of chlorine and nitrogen, which may produce an error of no less than 0.5 per cent. in the ratio of hydrogen to oxygen, whereas, to be of value in deciding the question as to the true atomic ratio of these two elements, the possible error should not exceed 0.06. A. H.

**A New Explosive Mixture.** By A. ANGELI (*Gazzetta*, 1894, **24**, ii, 52—58).—The action which occurs when a mixture of potassium nitrate, potassium carbonate and sulphur explodes is usually represented by the equation



On substituting potassium nitrite for the nitrate, a mixture is obtained which explodes in much the same way as the above. It is therefore probable that, during the fusion preceding the explosion, potassium nitrite is formed by the reducing action of potassium sulphide, which, in turn, owes its formation to the interaction of the potassium carbonate and sulphur.

A mixture of potassium nitrate with hypophosphite detonates in a similar manner, and potassium nitrite is found in the product obtained on cautiously melting potassium nitrate and hypophosphite together; the same is true of mixtures of nitrates and thiocyanates. On heating a mixture of sodium thiocyanate with potassium nitrate, it first melts and then deflagrates slightly, whilst a mixture of the thiocyanate with potassium nitrite detonates violently. W. J. P.

**Hyposulphurous acid.** By E. SCHÄR (*Ber.*, 1894, **27**, 2714—2722).—Attention is drawn to the fact, hitherto overlooked, that Schönbein had prepared hyposulphurous (hydrosulphurous) acid and investigated

many of its properties, several years before Schützenberger occupied himself with the subject. Schönbein found that when an indigo solution has been bleached with hyposulphurous acid, the colour can be restored, not only by oxidising, but also by reducing, agents, and even by heating in the absence of air. He thought, in consequence, that the original loss of colour must be due to the formation of an unstable compound of the colouring matter with the hyposulphurous acid. The author has repeated and extended Schönbein's experiments, and confirmed his results; he also is of opinion that the decolorisation of indigo by hyposulphurous acid cannot be explained satisfactorily as a reduction of the colouring matter. C. F. B.

**Electrolysis of Nitrosylsulphuric acid in Sulphuric acid Solution.** By A. GURCMAN (*Zeit. anorg. Chem.*, 1894, **7**, 161—166).—The apparatus employed for the electrolysis is so arranged that the electrodes are separated by a narrow tube in order that diffusion may be prevented as much as possible. A current of 4 volts, and not more than 0.1 ampère, is used. In the case of a solution containing 0.00316 gram of nitrous anhydride per 1 c.c., and using sulphuric acid of sp. gr. = 1.837, gas is evolved more quickly at the positive than at the negative pole, but the amount of gas evolved at the negative pole soon becomes greater than that at the positive pole. The liquid then becomes violet, and, after 40 hours' action, the evolution of gas at the negative pole ceases. As the electrolysis proceeds, the amount of nitric oxide evolved at the negative pole gradually diminishes; even when the amount has become very small, the solution still contains nitrosylsulphuric acid. The positive ions of the nitrosylsulphuric acid, NO and H, are liberated at the negative pole, the negative ion,  $\text{SO}_4$ , wanders to the positive pole and is split up into O and  $\text{SO}_3$ ; the latter then re-forms sulphuric acid. The oxygen oxidises a portion of the nitrosylsulphuric acid to nitric acid, the latter being reduced by the nitric oxide to nitrous acid, which then regenerates nitrosylsulphuric acid. Neither ammonia nor hydroxylamine are formed during the electrolysis.

With a solution containing 0.00326 gram of nitrous anhydride per 1 c.c., and using sulphuric acid of sp. gr. = 1.65, the electrolysis proceeds in a similar manner, but, after electrolysis, the residual acid contains no nitrous acid. E. C. R.

**Metallic Double Salts of Diammonium and Diamide.** By T. CURTIUS and F. SCHRADER (*J. pr. Chem.*, 1894, [2], **50**, 311—346).—Hydrazine unites with either one or two equivalents of an acid to form salts. The compounds with two equivalents may be looked on as containing a bivalent radicle, diammonium,  $(\text{N}_2\text{H}_6)''$ , related to the metals of the alkaline earths in the same way as the ammonium radicle is related to the alkali metals.

The salts containing one equivalent of acid are more stable than the others, and correspond with the very stable hydrate,  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ . These salts form a number of crystalline double salts with the sulphates and chlorides of many of the metals, but do not appear to be capable of forming alums. The following salts have been prepared.

1. Double sulphates. These are of the general formula



in which R may be Cu, Co, Ni, Fe (ous), Mn, Zn, or Cd.

These salts are all sparingly soluble in water, and differ from the corresponding ammonium salts [such as  $(\text{NH}_4)_2\text{SO}_4\cdot\text{NiSO}_4 + 6\text{H}_2\text{O}$ ] by containing no water of crystallisation. They are all obtained in the form of crystalline precipitates by mixing solutions of the two component salts.

2. Double chlorides. These are of the types  $\text{N}_2\text{H}_5\text{Cl}\cdot\text{RCl}_2$  and  $2\text{N}_2\text{H}_5\text{Cl}\cdot\text{RCl}_2$ .

*Diammonium mercuric chloride*,  $2\text{N}_2\text{H}_5\text{Cl}\cdot\text{HgCl}_2$ , is readily soluble, and may be recrystallised from water or alcohol. It forms well-developed, six-sided prisms, which become opaque in the air, and melt at  $178^\circ$  without decomposing. *Diammonium cadmium chloride*,  $\text{N}_2\text{H}_5\text{Cl}\cdot\text{CdCl}_2$ , forms delicate needles, whilst the *bi-salt*, containing two molecules of hydrazine hydrochloride,  $2\text{N}_2\text{H}_5\text{Cl}\cdot\text{CdCl}_2 + 4\text{H}_2\text{O}$ , separates in coarse prisms. *Diammonium zinc chloride*,  $\text{N}_2\text{H}_5\text{Cl}\cdot\text{ZnCl}_2$ , forms hygroscopic, six-sided prisms, melting between  $180^\circ$  and  $185^\circ$ . The *bi-salt*,  $2\text{N}_2\text{H}_5\text{Cl}\cdot\text{ZnCl}_2$ , crystallises in brittle, white, deliquescent needles, melting at  $135^\circ$ , and is difficult to prepare pure. The two double salts with stannous chloride are difficult to separate. The salt,  $\text{N}_2\text{H}_5\text{Cl}\cdot\text{SnCl}_2$ , crystallises in large, nacreous plates, melting at  $105^\circ$ ; the salt,  $2\text{N}_2\text{H}_5\text{Cl}\cdot\text{SnCl}_2$ , is very hygroscopic, and melts at  $55-60^\circ$ .

Hydrazine also forms a series of salts analogous to the ammonia compounds, as ammonionickel sulphate,  $\text{NiSO}_4\cdot 6\text{NH}_3$ , and ammoniozinc chloride,  $\text{ZnCl}_2\cdot 4\text{NH}_3$ .

When diammonium copper sulphate is dissolved in ammonia, the cupric salt is reduced to a cuprous salt, and nitrogen is rapidly evolved. The double salts of iron, manganese, mercury, and tin behave in a similar or analogous manner, whilst those of nickel, zinc, and cadmium form double salts,  $\text{NiSO}_4\cdot 3\text{N}_2\text{H}_4$ ,  $\text{ZnSO}_4\cdot 2\text{N}_2\text{H}_4$ ,  $\text{ZnCl}_2\cdot 2\text{N}_2\text{H}_4$ , and  $\text{CdCl}_2\cdot 2\text{N}_2\text{H}_4 + \text{H}_2\text{O}$ , which may also be prepared by adding hydrazine hydrate to a solution of the metallic salt.

It has hitherto been found impossible to prepare free hydrazine from any of these salts; the double zinc chloride, for example, does not yield any reducing substance when heated, but evolves ammonia. Researches in this direction are being continued. Hydrazine hydrate reduces molybdenum trioxide to the dioxide, does not affect tungstic acid, and reduces chromates and ferric salts to the corresponding lower oxides.

Hydrazine hydrate in the pure state can be preserved without undergoing any alteration, whereas its dilute solution rapidly loses its characteristic properties, even when kept in a sealed tube. The exact nature of the decomposition has not yet been made out.

A. H.

### Action of Nitric Oxide on Metals at High Temperatures.

By F. EMICH (*Monatsh.*, 1894, 15, 375-390; compare Abstr., 1892, 940; 1893, ii, 66).—The author generally confirms the results obtained by Sabatier and Senderens (Abstr., 1892, 1151 and 1271), and concludes

that the action of nitric oxide on the metals closely resembles, but is much slower than, that of oxygen, provided the temperature of the former gas is kept below the point at which its decomposition commences. Experiments with copper, zinc, cadmium, mercury, tin, lead, chromium, molybdenum, tungsten, uranium, manganese, iron, nickel, cobalt, titanium, and vanadium show that only three of these metals, namely, copper, lead, and vanadium, give products ( $\text{Cu}_2\text{O}$ ,  $\text{PbO}$ , and  $\text{Vd}_2\text{O}_3$  respectively) different from those obtained on heating them in a current of oxygen. In the case of mercury, the metal is not affected by nitric oxide at or below the temperature at which it boils.

G. T. M.

**Nitrous Anhydride.** By G. LUNGE and G. PORSCHNEW (*Zeit. anorg. Chem.*, 1894, **7**, 209–250) — These investigations were carried out in order to settle the question of the existence or non-existence of nitrous anhydride in the gaseous state. All conceivable precautions were taken to obtain pure materials for the investigation and to avoid sources of error, and many of the experiments made by previous investigators were repeated with additional precautions. The composition of the nitrogen oxides was determined by absorbing them by sulphuric acid, and either, *a*, estimating the total weight and total nitrogen, or, *b*, estimating the total nitrogen, and the amount of oxygen (in the form of permanganate) needed for complete oxidation.

1. *Action of Oxygen on excess of Nitric Oxide.*—Special precautions were taken to ensure thorough mixing of the gases. In no case did any oxygen remain uncombined, the whole quantity employed being found in the absorbed nitrogen oxides.

2. *Behaviour of a Mixture of Nitric Oxide and Peroxide towards Sulphuric acid.*—Nitric peroxide is well known to be readily absorbed by strong sulphuric acid, whilst nitric oxide is scarcely absorbed at all by that acid. In mixtures, nitric oxide was found to be readily absorbed when not present in excess of the proportion  $\text{NO}:\text{NO}_2::1:1$ . The absorption by sulphuric acid gives, therefore, no indication whether a gas is nitrous anhydride or a mixture of nitric oxide and peroxide in molecular proportion.

*Action of excess of Oxygen on Volatilising Nitrous Anhydride.*—The results showed that when excess of oxygen was present the whole of the nitrogen oxides (nitrous anhydride?) was converted into peroxide. The results obtained by Lunge, which seemed to show a resistant power of the  $\text{N}_2\text{O}_3$  molecule to further addition of free oxygen, were probably due to incomplete mixing of the reacting gases.

*Action of Nitric Oxide on Nitric Peroxide.*—Above  $28^\circ$ , no contraction, and consequently no combination, of the two gases could be observed when they were mixed. At  $-21^\circ$  and below, nitric oxide is freely absorbed by liquid nitric peroxide with formation of a blue liquid having the composition  $\text{N}_2\text{O}_3$ ; mixtures of the two oxides, when cooled to  $-21^\circ$ , yield the same blue liquid. These results are in contradiction to those of Hasenbach (*J. pr. Chem.*, 1871, [2], **4**, 1) and of Ramsay (*Trans.*, 1890, 590). Ramsay states that by passing nitric oxide through liquid nitric peroxide only about 3.5 per cent. of the latter is absorbed. He estimated this absorption, however, by the gain in

weight of the peroxide, and did not allow for the loss of weight due to nitric peroxide carried away by the escaping nitric oxide. The blue liquid has the exact composition  $N_2O_3$ , and when exposed in sealed tubes to the ordinary temperature the colour changes to green—the colour of liquid nitric peroxide. From this, the authors conclude that nitrous anhydride exists as a well-characterised chemical compound at  $-21^\circ$ , but that at ordinary temperatures (that is, above its boiling point) partial decomposition sets in, even under pressure, and whilst it is still in the liquid state.

*Vapour Density Determinations of Volatilised Nitrous Anhydride.*—Very careful determinations at ordinary temperatures and in vacuous vessels failed to show any excess in density over that of a mixture of nitric oxide and peroxide. The density was determined by the weight and pressure as registered by a manometer formed of a Hempel burette partly filled with carbonic anhydride. L. T. T.

**Formation of Hydrogen Phosphide.** By J. W. RETGERS (*Zeit. anorg. Chem.*, 1894, **7**, 265–266).—Based on some very old experiments of Fourcroy and Vauquelin, the text-books state that free hydrogen cannot be made to combine directly with phosphorus. The author finds that if a stream of hydrogen is passed over heated amorphous phosphorus, gaseous hydrogen phosphide is formed. The liquid and solid compounds are, at the same time, produced in small quantities. L. T. T.

**Thiohypophosphates.** By C. FRIEDEL (*Compt. rend.*, 1894, **119**, 260–264).—When various metals are heated with the calculated proportion of phosphorus pentasulphide, or, better, amorphous phosphorus and sulphur, thiohypophosphates are obtained pure and in crystals. In some cases any excess of phosphorus sulphide can be removed by boiling with sodium hydroxide solution, or by heating out of contact with air, when the sulphide sublimes; but purification is always difficult, and the best results are only obtained by using the calculated quantities of materials.

*Iron thiohypophosphate*,  $Fe_2P_2S_6$ , forms brilliant, greyish-black, hexagonal lamellæ resembling those of graphite or specular hematite. The lamellæ, when very thin, are brown by transmitted light, and have no action on parallel polarised light. The compound is attacked by nitric acid, but more easily by a mixture of the acid with potassium chlorate.

The *aluminium* compound forms elongated, white lamellæ, which act on polarised light; it alters rapidly when exposed to air, and is decomposed by water with evolution of hydrogen sulphide. The *zinc* salt is pale yellow, and is difficult to obtain in a state of purity. The *copper* salt,  $Cu_2P_2S_6$ , forms small, acicular crystals, which act strongly on polarised light. The *lead* salt is purified by boiling for some time with water, and then forms an orange-yellow, crystalline powder, which acts strongly on polarised light, and is not decomposed by water. The *silver* salt is sulphur-yellow; at a dull red heat, it burns with a flame like that of phosphorus, and leaves a brown, brittle residue. The *mercury* salt,  $Hg_2P_2S_6$ , forms sulphur-yellow



lamellæ, which act strongly on polarised light, and with a convergent beam shows rings. This compound is slowly decomposed by boiling water, and more rapidly by potassium hydroxide solution, a residue of mercuric sulphide being left. In presence of an excess of phosphorus sulphide, the compound can be sublimed, but it decomposes if strongly heated. When exposed to light, it gradually blackens.

Tin yields two compounds,  $\text{Sn}_3\text{P}_2\text{S}_6$  and  $\text{SnP}_2\text{S}_6$ , according to the proportion of tin employed; the first is orange-yellow, is decomposed by boiling water with evolution of hydrogen sulphide, and dissolves completely in concentrated potassium hydroxide solution. The second compound forms yellowish-brown radiating crystals, which alter when exposed to air, becoming yellow and opaque, and giving off hydrogen sulphide.

C. H. B.

**Sodium Pyrophosphates.** By T. SALZER (*Arch. Pharm.*, 1894, **232**, 365—375).—*Trisodium hydrogen pyrophosphate*,  $\text{Na}_3\text{HP}_2\text{O}_7 + \text{H}_2\text{O}$ , is prepared by evaporating a solution of the tetrasodium salt (13·5 grams) and the disodium salt (10 grams) in water (50 grams); it forms small crystals, is soluble in three parts of water at the ordinary temperature, is neutral to litmus, and with silver nitrate gives silver pyrophosphate,  $\text{Ag}_4\text{P}_2\text{O}_7$ . A salt of similar composition, but containing  $7\text{H}_2\text{O}$ , and crystallising in prisms, is formed when the disodium salt is employed in slight excess, and the solution gently warmed. It was only obtained in small quantity. *Sodium trihydrogen pyrophosphate*,  $\text{NaH}_3\text{P}_2\text{O}_7$ , mixed with metaphosphoric acid, was obtained from soda and pyrophosphoric acid. Attempts to prepare sodium tetrphosphate,  $\text{Na}_6\text{P}_4\text{O}_{13}$ , by heating trisodium hydrogen pyrophosphate were unsuccessful. A comparison of Fleitmann and Henneberg's and Uelsmann's sodium tetrphosphates shows that they are different; the former is probably a mixture, it crystallises in thin plates, and decomposes into disodium hydrogen phosphate and sodium dihydrogen phosphate in presence of water; the latter can be readily recrystallised, is deposited in small needles, and is not decomposed by the prolonged action of water.

J. B. T.

**Orthoplumbates of the Alkaline Earths.** By G. KASSNER (*Arch. Pharm.*, 1894, **232**, 375—387).—Calcium plumbate,  $\text{Ca}_2\text{PbO}_4$ , combines with water at the ordinary temperature; the mixture solidifies, the colour changes from yellowish-red to pale yellow, and almost colourless, microscopic, transparent crystals of a *hydrate* containing  $4\text{H}_2\text{O}$  are formed. With dilute nitric acid, the crystals turn brown, and finally become pulverulent.

By the action of water at  $150^\circ$ , a yellowish-green, voluminous powder is formed; with acids at the ordinary temperature, it darkens, becoming finally black; boiling dilute acetic acid rapidly produces the same change. Its composition agrees with that of a hydrate with  $2\text{H}_2\text{O}$ , but it appears to be a mixture of calcium hydroxide (3 mols.) and a hydrogen calcium diplumbate,  $\text{H}_2\text{CaPb}_2\text{O}_6$ , resulting from the hydrolysis of the orthoplumbate; the calcium hydroxide is extracted by washing with water free from carbonic anhydride; the residual diplumbate is yellow, and relatively

stable towards acids. On one occasion, by the action of dilute nitric acid on the diplumbate, hydrogen calcium triplumbate,  $\text{H}_2\text{CaPb}_3\text{O}_8$ , was formed as a greyish-brown powder resembling the diplumbate in general properties. Both compounds decompose suddenly at a definite temperature into oxygen and lead dioxide. Attention is called to the analogy between the highest oxidation products of lead, silicon, and carbon, which is emphasised by the discovery of these complex acids of lead.

J. B. T.

**Volatility of Mercuric Chloride.** By H. ARCTOWSKI (*Zeit. anorg. Chem.*, 1894, **7**, 167—175).—The author shows that mercuric chloride is decidedly volatile at the ordinary temperature, and has also determined the volatility at various temperatures from  $56^\circ$  to  $125^\circ$ , keeping the other conditions constant. Taking the temperatures as abscissæ, and the amounts of chloride volatilised as ordinates, a curve is obtained for the relative volatility which is asymptotic to the temperature-axis.

E. C. R.

**Cerium Compounds.** By L. M. DENNIS and W. H. MAGEE (*Zeit. anorg. Chem.*, 1894, **7**, 250—264).—The authors, having obtained considerable quantities of allanite, intend to carefully investigate the derivatives of cerium. For the separation of cerium from the other earths of this group, the best method is a modification of Debray's fusion with potassium nitrate (*Abstr.*, 1883, 713). When employing potassium nitrate, the fusion point of the mixed nitrates is about  $325^\circ$ , and at this temperature traces of didymium nitrate are always decomposed, so that the insoluble cerium oxide left after treatment of the melt with water always contains didymium. The authors substitute a mixture of potassium and sodium nitrates in molecular proportion for the potassium nitrate. Such a mixture melts at  $231^\circ$  (Carnelly and Thomson, *Trans.*, 1888, 792). By this means the melting point of the mixed nitrates was reduced below  $230^\circ$ , and the decomposition could be carried out at  $300^\circ$ . No didymium nitrate was then decomposed, and the cerium oxide obtained after each fusion was free from impurity.

After trial of the various qualitative tests for cerium, the authors recommend Cleve's (*Abstr.*, 1885, 635) and Boisbaudran's (*ibid.*) method of adding excess of ammonia, and then hydrogen peroxide, to the solution. The orange precipitate or coloration can be detected with as little as 0.005 milligram of cerium oxide.

In attempting to obtain a tetrachloride by saturating with dry chlorine, at a low temperature, a concentrated hydrochloric solution of cerium oxide, a *chloride*,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ , was obtained; the same salt was formed when a stream of dry hydrogen chloride was substituted for the chlorine. The salt forms orthorhombic crystals showing the axial ratios  $a : b : c = 0.80834 : 1 : 1.44187$ . It loses part of its water of crystallisation in a vacuum over dehydrating agents, but is stable in the air. It appears to be different from the salt,  $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$ , already known.

Cerous hydroxide when pure is white, but when moist readily absorbs oxygen, becoming first purple and then yellow, the latter

coloured substance yielding, on ignition, ceric oxide. The purple hydrate is undoubtedly in an intermediate stage of oxidation.

L. T. T.

**Nitrogen Compounds of Manganese.** By O. PRELINGER (*Monatsh.*, 1894, 15, 391—401).—*Pentamanganese nitride*,  $Mn_5N_2$ , and *trimanganese nitride*,  $Mn_3N_2$ , are obtained on passing nitrogen and ammonia respectively over finely-divided manganese, heated to redness in a hard glass tube. The former has a dull, metallic lustre, and, when finely divided, is somewhat darker than powdered manganese. On heating in a stream of hydrogen, ammonia is formed, whilst if hydrogen sulphide is substituted for the element, ammonium sulphide results. On treatment with ammonium chloride solution, ammonia, hydrogen, and the double chloride of manganese and ammonium are obtained, and on fusion with caustic alkali much ammonia is liberated. The compound,  $Mn_3N_2$ , forms a darker powder, but otherwise closely resembles the substance previously described. The author points out that the constitution of the two compounds may be explained by assuming the nitrogen to be pentavalent in the case of the pentamanganese nitride, and trivalent in that of the trimanganese nitride.

G. T. M.

**Manganese Steel.** By H. LE CHATELIER (*Compt. rend.*, 1894, 119, 272—274).—The manganese steel discovered by Hadfield is practically non-magnetic, and has a higher resistance than any other alloy of iron. Moreover, it is more malleable, the more highly it has been tempered. Hadfield has found that an allotropic modification, which is magnetic, can be obtained by heating the ordinary manganese steel at a high temperature for several days.

The author finds that the change from non-magnetic to magnetic metal takes place between  $500^\circ$  and  $650^\circ$ , and, at the most favourable temperature,  $550^\circ$ , the change is complete in an hour or two. In order to convert the magnetic metal to the non-magnetic, it must be heated at a temperature not lower than  $800^\circ$ , and must be cooled somewhat rapidly in order to prevent the reverse change between  $500^\circ$  and  $600^\circ$ . Since the rate of this latter change is very low, ordinary cooling in air is usually sufficient.

The electrical resistance of a wire, 1 mm. long and 1.4 mm. diameter, is as follows.

Temperature.....	$15^\circ$	$90^\circ$	$200^\circ$	$500^\circ$	$635^\circ$	$730^\circ$	$850^\circ$	$965^\circ$	$1020^\circ$
Resistance { non-magnetic	1.06	1.19	1.44	1.65	—	—	1.88	—	1.97
{ magnetic....	0.88	0.99	1.27	1.50	1.7	1.79	—	1.93	1.97

The two curves touch at  $740^\circ$ , and coincide above this temperature, and hence this is the temperature of transformation of the two varieties of metal. This temperature is, however, also that at which soft iron becomes non-magnetic. It would seem, therefore, that manganese steel is a mixture of iron with a definite compound of iron and manganese, the latter being non-magnetic under any conditions. The iron undergoes the normal changes, but they take place more slowly, in consequence of the presence of the manganese compound.

The expansion of the two varieties of manganese steel is the same, and hence it would follow that there is no change of dimensions at the point of transformation. The following table gives the expansion of a rod 100 mm. long.

Temperature..	230°	500°	680°	830°	990°	1060°.
Expansion....	0.35	0.67	1.05	1.43	1.97	2.09 mm.

Manganese steel tempered in water shows, at once, when annealed, a definite contraction of 0.4 mm. on 100 mm. C. H. B.

**Chemical Behaviour of Arsenical Pyrites.** By T. M. LIGHTFOOT (*J. Amer. Chem. Soc.*, 1894, 16, 624—633).—The author has tried the action of solutions of potassium permanganate, of different strengths and at different temperatures, on arsenical pyrites, and has tabulated the results. Potassium permanganate partially oxidises the sulphur, but even at the boiling heat nothing like a complete oxidation takes place. The sulphur oxidised was estimated in the filtrate by the usual process.

Hydrogen chloride at a high temperature does not expel large quantities of sulphur, but removes considerable amounts of arsenic. In these experiments, the sulphur left in the boat was oxidised in the ordinary way, and deducted from the total sulphur, the difference being the sulphur volatilised.

Solution of copper sulphate under pressure dissolved but little ferrous iron, which goes to prove that the mineral contains the iron in the ferric state. A little green copper arsenate was also formed in the reaction. L. DE K.

**Action of Ferric Sulphate on Potassium Iodide and Hydriodic acid.** By K. SEUBERT and R. ROHRER (*Zeit. anorg. Chem.*, 1894, 7, 137—153).—The action between ferric sulphate and potassium and hydrogen iodides takes place in a manner very similar to that described by Seubert and Dorrer for ferric chloride (*Abstr.*, 1894, ii, 191). The reaction with one equivalent of ferric sulphate,  $\frac{1}{2}\text{Fe}_2(\text{SO}_4)_3$ , and varying proportions of potassium iodide, approaches the theoretical when 20 mols. of potassium iodide are present. The yield is then 97 per cent., and any further increase in the proportion of potassium iodide produces no increase in the amount of free iodine. When the results are compared with those obtained with ferric chloride, it is evident that the action is much slower, and for small excesses of potassium iodide is never so complete. The results obtained with the proportion  $\text{FeCl}_3 : \text{KI}$  correspond with those obtained with the proportion  $\text{Fe}_2(\text{SO}_4)_3 : 4\text{KI}$ . When the action is allowed to proceed for 18 hours, using an equivalent of ferric sulphate, and varying proportions of potassium iodide, the amount of iodine liberated is at first much less than the amount liberated when ferric chloride is used, but the difference becomes small for 6 mols. KI, and disappears for 10 mols.

With 1 mol. of potassium iodide and varying proportions of ferric sulphate, the action is also much slower than with ferric chloride; and the numbers obtained with the proportions  $2\text{KI} : 4\text{Fe}_2(\text{SO}_4)_3$

and  $2\text{KI} : 10\text{Fe}(\text{SO}_4)_3$  agree with those obtained for the proportions  $\text{KI} : \text{FeCl}_3$  and  $\text{KI} : 2\text{FeCl}_3$  respectively.

The action between ferric sulphate and hydrogen iodide is also slower and less complete than that between ferric chloride and hydrogen iodide.

It is evident that the reaction  $\text{Fe}_2(\text{SO}_4)_3 + 2\text{KI} = 2\text{FeSO}_4 + \text{K}_2(\text{SO}_4) + \text{I}_2$  is a reversible one when none of the products are removed from the sphere of action. And experiments with mixtures containing various molecular proportions of ferrous sulphate potassium iodide, iodine, and potassium sulphate, after remaining 144 hours, always contained an amount of iodine corresponding with that liberated by an equivalent mixture of ferric sulphate and potassium iodide.

E. C. R.

**Attempt to prepare Molybdenum Hexachloride.** By E. F. SMITH and H. C. BURR (*J. Amer. Chem. Soc.*, 1894, **16**, 577—578).—The authors thought that if a partially chlorinated molybdic acid were exposed to chlorinating agents, the residual oxygen might be removed, and that then perhaps the hexachloride might be obtained as a final product. To this end, molybdenyl chloride,  $\text{MoO}_2\text{Cl}_2$ , was mixed with an equivalent quantity of phosphorus pentachloride, and heated in a sealed tube, in the presence of chlorine, at  $170^\circ$ . On cooling, it was found that the tube contained a mass of greenish-black crystals; these, when freed from phosphorus oxychloride by distillation in a current of chlorine, yielded a product which, on analysis, gave figures approximating more to the pentachloride than to the hexachloride. The experiment was repeated, silicon tetrachloride being substituted for the phosphorus compound. The crystalline product was quickly removed to a boat, and distilled in an atmosphere of carbonic anhydride. The brown vapours condensed in the colder portions of the tube, and on analysis gave results varying between those required by the tetrachloride and pentachloride.

The authors have not, however, given up all hope of preparing the hexachloride. They have observed that metallic molybdenum rapidly acts on ferric chloride solution with reduction of the ferric salt, and dissolves as a hexad. Further experiments will be made to get it in the solid state.

L. DE K.

**Salts of Sulphomolybdic acid.** By A. ROSENHEIM (*Zeit. anorg. Chem.*, 1894, **7**, 176—184).—The salts described in this communication have been previously prepared by Péchard (*Abstr.*, 1893, ii, 530). The author confirms the results previously obtained as to their properties; but his analytical results do not agree with the composition of the salts assigned to them by Péchard. The ammonium salt has the composition  $3(\text{NH}_4)_2\text{O} \cdot 2\text{SO}_2 \cdot 8\text{MO}_3 + 5\text{H}_2\text{O}$ , the potassium salt is  $4\text{K}_2\text{O} \cdot 4\text{SO}_2 \cdot 9\text{MO}_3 + 5\text{H}_2\text{O}$ , whilst the sodium salt has the composition  $9\text{Na}_2\text{O} \cdot 8\text{SO}_2 \cdot 20\text{MO}_3 + 37\text{H}_2\text{O}$ .

E. C. R.

**Complex Inorganic Acids.** By V. ALVISI (*Gazzetta*, 1894, **24**, i, 523).—On warming phosphomolybdic acid with hydrofluoric acid solution, the yellow colour disappears, and the solution no longer gives a

precipitate with ammonium nitrate; on concentration, the yellow colour reappears, and ammonium nitrate then precipitates the salt  $\text{MoO}_3 \cdot 2\text{NH}_4\text{F}$ .

Ammonium phosphomolybdate, when warmed with concentrated hydrofluoric acid, yields monammonium fluoroxymolybdate (compare Mauro, *Abstr.*, 1891, 18).

Neutral potassium fluoroxymolybdate is deposited on mixing solutions of potassium hydrogen fluoride and phosphomolybdic acid. Ammonium fluoride acts on ammonium phosphomolybdate with formation of the salt  $\text{MoO}_3 \cdot \text{NH}_4\text{F}$ , and on phosphomolybdic acid, giving the salt  $\text{MoO}_3 \cdot 2\text{NH}_4\text{F}$  and normal ammonium fluoroxymolybdate  $\text{W. J. P.}$

**A New Oxysulphide of Tin.** By F. W. SCHMIDT (*Ber.*, 1894, **27**, 2739—2743).—When stannic sulphide, obtained in the usual way by the action of hydrogen sulphide on a solution of stannic chloride, is allowed to remain in contact with ammonia, it dissolves, forming a solution, which, on acidification, yields a very voluminous white precipitate. The same substance may be obtained by digesting stannic sulphide with ammonium carbonate solution, filtering, and acidifying; about 10 per cent. of the stannic sulphide is dissolved.

This compound when freed from sulphur by treatment with carbon bisulphide, has the composition  $\text{Sn}_2\text{S}_3\text{O} + 11\text{H}_2\text{O}$ , is easily and completely soluble in ammonium carbonate, and is also slowly soluble in water. When dried, the white mass gradually loses its property of dissolving in ammonium carbonate solution, and becomes amber-yellow, but, even after preservation for a year, this yellow mass dissolves readily in ammonia, and the solution thus obtained deposits the white compound when excess of acid is added.

The partial solubility of stannic sulphide in ammonium carbonate solution is of great analytical importance, as this reagent is often used to separate the sulphides of tin and arsenic. A. H.

**New Method of Extracting Gold from Auriferous Ores by means of Bromine.** By C. LOSSEN (*Ber.*, 1894, **27**, 2726—2727).—Hitherto bromine has not been used for this purpose, as it could not be readily recovered, and the cost of the process was consequently too great. The author electrolyses a solution of potassium bromide, and obtains an alkaline solution which contains hypobromite and bromate, and which is capable of dissolving gold. The ore is treated with excess of this solution in rotating cylinders, the solution is then filtered, the gold is precipitated by passage over a mixture of iron and coal, and the solution, which now contains mainly potassium bromide, is electrolysed and again used for extraction. C. F. B.

## Mineralogical Chemistry.

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**Native Iron.** By G. C. HOFFMANN (*Zeit. Kryst. Min.*, 1894, **33**, 507; from *Ann. Rep. Geol. Surv., Canada*, **5**, part R).—Native iron occurs as a constituent of a thin crust of oolitic structure on quartzite on the north shore of St. Joseph's Island, Lake Huron, Ontario. An analysis of the crust gave

Metallic grains.	Limonite.	Siliceous matter.
58.85	39.73	1.42

The metallic spherules varied from microscopic minuteness to a diameter of 0.37 mm., and gave the following results on analysis.

Fe.	Mn.	Ni.	Co.	Cu.	S.	P.	Insoluble.
88.00	0.51	0.10	0.21	0.09	0.12	0.96	9.76

From this, the author concludes that the metallic portion of these grains contains 97.79 per cent. of iron, and that they were formed by reduction of an iron salt by means of an organic material.

B. H. B.

**Mineral Wax from Kaluga.** By W. ALEXÉEFF (*Jahrb. f. Min.*, 1894, ii, Ref. 231; from *Verhand. russ. kais. min. Ges. St. Petersburg*, **29**, 201—203).—This new substance, presenting the external characteristics of ozokerite, was found in the peat of the Russian province of Kaluga. It is almost insoluble in alcohol and benzene. Its sp. gr. is 0.950, and its melting point between 64° and 65°. Analysis yielded

C.	H.	O.
75.5	12.5	12.0

On distillation, water was formed and a liquid with a sp. gr. of 0.786, and a boiling point of 240°; analysis gave C = 83.4; H = 13.8 per cent.

B. H. B.

**Grahamite from Texas.** By E. T. DUMBLE (*Zeit. Kryst. Min.*, 1892, 1894, **33**, 509; from *Trans. Amer. Inst., M.E.*, **21**, 601—605).—Grahamite, an asphalt-like substance, occurs in thin veins and in masses in the tertiary rocks near Webb Bluff, on the Rio Grande (I), and at O'Quinn and Buckner's Creeks (II). Analyses gave the following results.

H <sub>2</sub> O.	Volatile matter.	Fixed carbon.	Ash.	Total.
I. 0.30	44.00	52.80	2.90	100.00
II. —	57.90	37.70	4.40	100.00

C.	H.	N.	O.	S.	Ash.	H <sub>2</sub> O.
I. 78.65	7.50	0.15	5.08	5.42	2.90	0.30
II. 76.19	6.61	0.39	5.15	7.45	4.21	—

B. H. B.

**Chemical Constitution of Iron Pyrites.** By J. LOCZKA (*Zeit. Kryst. Min.*, 1894, **33**, 501).—Seeing that an identical anhydrous ferric

sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , is obtained on treatment with concentrated boiling sulphuric acid, both from iron pyrites and from ferrous compounds, the author concludes that iron pyrites is a ferrous compound. This view is supported by the fact that, on weathering, iron pyrites is decomposed into ferrous sulphate and sulphuric acid. The formula of iron pyrites should therefore be  $\text{Fe} < \frac{\text{S}}{\text{S}}$ .

B. H. B.

**Andorite, a New Hungarian Silver Ore.** By J. A. KRENNER (*Zeit. Kryst. Min.*, 1894, **33**, 497—499).—This new and rare mineral was found with antimonite, quartz, and zinc-blende in the main vein at Felsöbánya. It is a dark, leaden-grey to black mineral, crystallising in the rhombic system, and yielding on analysis the following results.

Sb.	S.	Pb.	Ag.	Cu.	Fe.	Insoluble.
41.91	23.32	22.07	11.31	0.69	0.70	0.04

The formula is  $\text{Sb}_6\text{S}_{12}\text{Pb}_2\text{Ag}_2$ .

B. H. B.

**Preparation of Artificial Anatase and Rutile.** By B. DOSS (*Jahrb. f. Min.*, 1894, ii, Mem., 147—206).—Shortly after G. Rose's announcement, in 1867, that tabular anatase was formed by saturating a microcosmic salt bead with artificial or with natural titaniferous acid, a correction was made by A. Knop, who stated that the crystals in question contained phosphoric acid, and had a sp. gr. of only 2.9. Further, G. Wunder showed that besides phosphoric anhydride, sodium was also present. In the course of an investigation of the alteration products of a Saxon syenite, the author found it necessary to compare undoubted specimens of anatase and of rutile. For this purpose, artificial material was required, and the author obtained artificial rutile by G. Rose's method of saturating a borax bead with titanous anhydride. His experiments, made with the object of obtaining anatase with a microcosmic salt bead, were successful, but with a borax bead the results were negative. Rutile, on the other hand, could be obtained in either case.

B. H. B.

**New Tin Mineral from the Black Hills.** By T. ULKE (*Zeit. Kryst. Min.*, 1894, **33**, 509; from *Trans. Amer. Inst., M.E.*, 1892, **21**, 240).—At the Etta Mine, in the Black Hills of Dakota, there occurs in quartz veins a yellowish, earthy substance, accompanied by cassiterite. It contains 60 per cent. of tin, 12 per cent. of copper, and 8 per cent. of water. The author assigns to it the formula  $4\text{SnO}_2 + \text{Cu}_2\text{Sn}(\text{OH})_6$ , and the name of *cuprocassiterite*. The mineral has, however, been investigated also by W. P. Headen (*Amer. J. Sci.*, 1893, [3], **45**, 105), who considers it to be a mixture due to the decomposition of tin pyrites.

B. H. B.

**Nickel Arsenide.** By E. WALLER and A. J. MOSES (*School of Mines Quarterly*, 1892, **14**, 49—51).—A probably new nickel arsenide was found at a mine 18 miles west of Silver City, New Mexico. Its composition was found to be as follows.



SiO <sub>2</sub> .	Pb.	Ag.	As.	Ni.	Co.	Fe.
4.56	trace	8.38	67.37	11.12	5.13	2.64

This corresponds with the formula  $RAs_3$ , in which R represents  $\frac{4}{7}Ni$ ,  $\frac{2}{7}Co$ , and  $\frac{1}{7}Fe$ . The mineral is thus of the type of skutterudite  $CoAs_3$ .  
B. H. B.

**Apatite in a Laminated Graphite from Ceylon.** By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, 1894, **7**, 154—157).—The apatite occurred as an ellipsoidal mass about the size of a walnut, and is of a beautiful, green colour. Analysis gave

P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
39.84	2.02	0.62	0.22	53.36	0.25	0.52	0.42
H <sub>2</sub> O.	Cl.	F.	Total.				
0.48	1.82	1.03	100.58				

This agrees with the formula  $P_3O_{12}(F, Cl, OH)Ca_5$ .  
E. C. R.

**Svabite and Adelite.** By H. SJÖGREN (*Jahrb. f. Min.*, 1894, ii, Ref., 237—238; from *Bull. geol. inst. univ. Upsala*, **1**, 1).—The author gives two analyses of svabite from the Harstig Mine and from the Jakobsberg Mine, near Nordmarken. The mineral occurs in granular hausmannite in yellowish-white to colourless masses. The formula deduced from the analyses is  $3As_2O_5, 9CaO, CaF_2$ .

Analyses of adelite from the Kittel Mine, from Moss Mine, and from Jakobsberg Mine gave results agreeing with the formula  $HO \cdot MgCaAsO_4$ , in which calcium is partially replaced by lead, manganese, and iron.  
B. H. B.

**Fergusonite from Ceylon.** By G. T. PRIOR (*Min. Mag.*, **10**, 234—238).—Accompanying the baddeleyite of Rakwana, in Ceylon, fragments of so-called yttrotantalite were found. The sp. gr. was 4.54 to 5.49, the hardness 5 to 6, and the colour dark brown. The mineral is very brittle, isotropic, and translucent, with yellowish-brown colour, in thin fragments. Analysis yielded the following results.

Nb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	UO <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Er <sub>2</sub> O <sub>3</sub> .	CaO.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
44.65	4.98	5.11	24.67	13.24	2.02	0.51	4.58	99.78

The mineral is thus fergusonite, and resembles in all its characters the fergusonite of Ytterby.  
B. H. B.

**Crystallochemical Theory of the Silicates.** By F. J. WILK (*Zeit. Kryst. Min.*, 1894, **33**, 379—450).—The author propounds an elaborate theory of the relation between the chemical and crystallographical characters of the silicates. On the basis of this theory, he gives the following crystallochemical classification of the silicates.

Class I. *Geolites*.—1. Plagioclase (anorthite, andesine, albite); microcline, orthoclase; spodumene, petalite, wollastonite; danburite,

leucophane, meliophane. 2. Scapolite (gehlenite, sarcolite); nepheline (cancrinite, davyn), milarite. 3. Leucite; sodalite (nosean, haunyn).

Class II. *Hydrogeolites* (Zeolites).—1. Datolite, prehnite; desmine (harmotome, phillipsite), heulandite (brewsterite, epistilbite); scolezite, natrolite (mesolite), thomsonite; laumontite (leonhardite); okenite (pectolite). 2. Apophyllite; chabasite (gmelinite, levyn, herschelite). 3. Analcime, faujasite, pollux.

Class III. *Phyllites*.—1. Muscovite (paragonite, margarite, lepidolite), biotite (meroxene, phlogopite, zinnwaldite), clintonite; clinocllore (pennine); talc, serpentine; pyrophyllite, kaolin. 2. Biotite (in part); prochlorite.

Class IV. *Amphoterolites*.—1. Axinite; epidote (piemontite), orthite (mosandrite), karpopholite (ardennite), zoisite (thulite); gadolinite (homilite), euclase; cordierite (pinite). 2. Tourmaline, cappeleinite (melanocerite, karyocerite, tritomite), endialyte; idocrase (melilite). 3. Garnet, helvine.

Class V. *Styloites*.—1. Sapphirine, cyanite, dumortierite, andalusite (sillimanite, xenolite), staurolite; topaz, bertrandite. 2. Beryl; thorite (orangite), zircon. 3. Zunyite.

Class VI. *Metallolites*.—1. Rhodonite, babingtonite, pyroxene (malacolite, diallage, diopside, augite), acmite (aegirine), woehlerite; amphibole (tremolite, grammatite, amphibole-anthophyllite, hornblende), arfvedsonite; titanite, guarinite, liövilleite; olivine (forsterite, hyalosiderite, fayalite, tephroite), monticellite, chondrodite (humite, klinohumite); calamine, cerite. 2. Willemite (troostite), phenacite, diophtase; pyrosmalite. 3. Eulytine.

B. H. B.

**Orthoclase from Canada.** By B. C. HINMAN (*School of Mines Quarterly*, 1892, **14**, 52).—A fine, cleavable felspar from 30 miles from Buckingham, Ottawa Co., Province of Quebec, yielded

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	CaO.	Na <sub>2</sub> O.
65·87	19·32	11·78	0·64	2·39

B. H. B.

**Neptunite, Epididymite, Katapleite and Ægirine from Greenland.** By G. FLINK (*Zeit. Kryst. Min.*, 1894, **33**, 344—367).—The author describes an interesting series of minerals from Greenland, the locality where they were obtained being thought to be in the vicinity of Julianehåb, in syenitic pegmatite veins. The minerals described are (1) neptunite, (2) epididymite, (3) katapleite, a mineral hitherto known only from Langesund, in Norway, and (4) ægirine, the mineral of most frequent occurrence at this new locality.

The new mineral, *neptunite*, occurs in monosymmetrical crystals, and has the following composition.

SiO <sub>2</sub> .	TiO <sub>2</sub> .	FeO.	MnO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
51·93	17·45	10·23	5·32	0·71	5·71	9·36

The composition of the new mineral, *epididymite*, is identical with that of the mineral *eudidymite*, discovered by Brögger, in Norway,

and may be represented by the formula  $\text{Si}_3\text{O}_8\text{BeNaH}$ . The crystals of eudidymite are, however, monosymmetrical, whilst those of epididymite are rhombic.

B. H. B.

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## Physiological Chemistry.

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**Percentage of Nitrogen in Red Blood Corpuscles in Health and Disease.** By R. v. JAKSCH (*Chem. Centr.*, 1894, i, 782; from *Zeit. Klin. Med.*, **24**, 429—440).—100 grams of healthy blood contains 22·6 grams of proteïd; in anæmia, this may sink to 10; the two factors concerned in this fall are the corpuscles and the plasma. 100 grams of red blood corpuscles contains in health 5·52 grams of nitrogen, corresponding with 34·5 grams of proteïd. In acute disease, the nitrogen may rise to 5·89, and in chronic diseases, not associated with anæmia, to 5·56. In pernicious anæmia, it may rise to 6·48, corresponding with 40·5 grams of proteïd; but other forms of anæmia, especially chlorosis, show a great diminution in the nitrogen of the red corpuscles. In leucæmia, the same is true.

W. D. H.

**The Blood in Anæmia.** By E. BIERNACKI (*Chem. Centr.*, 1894, i, 781—782; from *Zeit. Klin. Med.*, **24**, 460—511).—The investigation relates more particularly to the mineral constituents of the blood in various forms of anæmia, especially that produced by infectious diseases like typhoid and pneumonia. Anæmic blood contains more sodium and water, and less potassium, phosphorus, and iron, than healthy blood. The numbers given in regard to the sodium chloride are:—Healthy blood contains 0·441 to 0·468 per cent. of sodium chloride. In pathological blood, this number fell to 0·374—0·366, or rose to 0·509—0·653; the cases where the rise was noted were strongly hydræmic. The excretion of the salt in the alimentary tract and urine does not, however, vary.

W. D. H.

**Sugar in the Blood after Bleeding.** By F. SCHENCK (*Pflüger's Archiv*, 1894, **57**, 553—572).—Claude Bernard originally stated that loss of blood caused a rise of sugar in the residual blood. This was confirmed by v. Mering, and also in the present research, where a new method (removal of proteïds by mercuric chloride, and subsequent titration by Knapp's method) was employed. The rise of sugar begins immediately after bleeding, but cannot be recognised a few hours after. The source of the sugar is apparently the liver, as the rise does not occur if the liver is cut off from the circulation; it is more marked when ammonium carbonate is given, this drug stimulating glycogenesis, and is diminished by glycenol, which inhibits the change of glycogen into sugar.

W. D. H.

**Formation of Sulphuric acid in the Organism.** By W. J. SMITH (*Pflüger's Archiv*, 1894, **57**, 418—426).—A number of new experi-

ments are recorded which, together with those previously published, show that mercaptans like thio-acids are decomposed in the organism, and lead to an increase of sulphuric acid in the urine. Ethyl mercaptan is decomposed differently inside and outside the body, the union between sulphur and carbon being in the former case dissolved, in the latter not. The explanation of such a difference is postponed.

W. D. H.

**The Leucine of the Pancreatic Fermentation.** By R. COHN (*Ber.*, 1894, 27, 2727—2732).—Leucine, obtained by fermenting blood-fibrin with calves' pancreas, was not found to melt and partially sublime at 170°, as stated in all text-books; it melted and decomposed at 275—276°. This is about the melting point (under pressure) of inactive leucine, but the new modification differs from the latter in its greater solubility in water, in being feebly laevorotatory, and in the fact that it is completely destroyed by *Penicillium glaucum*. It is also more soluble in water than the pancreas-leucine hitherto described. The author suggests that not one leucine, but a series of such, is formed in the pancreatic fermentation.

C. F. B.

**Peptone in Urine.** By W. ROBITSCHKE (*Chem. Centr.*, 1894, i, 780; from *Zeit. Klin. Med.*, 24, 542—614).—Peptonurias found in many diseases, especially during suppuration, and also in phosphorus poisoning. Devoto's method is recommended for its detection.

W. D. H.

**Behaviour of the Aromatic Hydroxy Ketones in the Animal Organism.** By M. NENCKI (*Ber.*, 1894, 27, 2732—2736).—When resacetophenone is administered to dogs, their urine is found to contain resacetophenone-sulphuric acid and glycuronic acid. *Potassium resacetophenonesulphate* crystallises in white needles, and, by gentle warming with hydrochloric acid, is decomposed into resacetophenone and sulphuric acid. The free acid also forms white needles, and may be recrystallised from alcohol.

Parahydroxypropiophenone undergoes a similar change, but the corresponding acids have not been isolated. These hydroxyl-compounds therefore differ from acetophenone itself, which is converted into benzoic acid by oxidation in the system, and is excreted in the form of hippuric acid.

A. H.

## Chemistry of Vegetable Physiology and Agriculture.

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**The Separation of Oxygen by Cells containing Chromophyll.** By T. W. ENGELMANN (*Pflüger's Archiv*, 1894, **57**, 375—386).—In these researches, the bacterial method was employed, and the results, which are illustrated by coloured figures, were as follows.

Green plant cells give off oxygen in the light, the amount within wide limits varying with the illumination. The bacteria used need free oxygen for their movements, and within wide limits the amount of movement varies with the amount of oxygen. In cells with chromophyll granules, this test shows that the granules are the source of the oxygen; colourless protoplasm, cell membrane, and nucleus are not. Red light, which is that most absorbed by chlorophyll, leads to the greatest development of oxygen. The green pigment is not itself capable of so acting; it must be present in connection with the living stroma of the chlorophyll granule. Other chromophylls act similarly.

W. D. H.

**Hydrogen Peroxide in Green Plants.** By A. BACH (*Compt. rend.*, 1894, **119**, 286—288).—The author has investigated the applicability of the various reagents for hydrogen peroxide to the detection of this substance in the leaves of green plants or the extract from them.

Tetramethylparaphenylenediamine is coloured by calcium chloride and by glycerol owing to their absorption of oxygen, and is also affected by nitrous acid; on this account the results obtained are always open to question. Tincture of guaiacum in presence of diastase is difficult to use, and the results are uncertain. Potassium iodide and starch in presence of ferrous sulphate is affected by any unsaturated substances that can absorb iodine, and such substances are always present in the leaf extract. Titanic oxide dissolved in sulphuric acid gives, with tannin, the same coloration as with hydrogen peroxide, and tannin is always present in leaf extract. Uranium acetate is precipitated by albumin and by tannin, and the turbidity does not completely disappear on adding acetic acid. Potassium dichromate and ether is never very sensitive, and is much less sensitive in presence of a solution of tannin or an extract of leaves.

It follows that none of the ordinary reagents for hydrogen peroxide yield satisfactory results when applied to leaves or an extract of leaves.

C. H. B.

**Formation of Substance in Sea Algæ.** By A. HANSEN (*Bied. Centr.*, 1894, **23**, 544—545; from *Naturw. Rundsch.*, 1893, 73.).—The *Phæophyceæ* (especially *Dictyoma*) do not produce starch but fat. The substance found in the cells of the inner cell-layer of the thin sprouts, which Berthold supposed to be albuminous, gives the microchemical reaction of fat. The cells serve as a storing place for the fat which is produced in the assimilative tissues. Fat was also found in *Taonia atomaria* and in *Halysieris polypodioides*, whilst oil could be

detected in *Asperococcus hydroclathrus* and in *Cystoseira*. The production of substance in the *Florideæ* seems to be more complicated. The cells of the assimilative tissues of *Chondriopsis cœrulescens* contain a globular substance which reflects light in a peculiar manner, and, according to Kny, gives rise to the iridescence of this plant. Inasmuch as no oil or starch, &c., could be found in the cells, this substance is probably a food. It swells up in water, dissolves in alcohol, and becomes dark (but not black) when treated with osmic acid, and brown when treated with iodine.

A starch-like substance was only found in *Gracilaria* (a small species of *Florideæ*).

An examination of the dyes of sea algæ indicated that the red colour of the *Florideæ* is the albumin compound of a dye, like hæmoglobin. The green colour of the *Florideæ* can be separated into a yellow dye, and a green dye, probably ordinary chlorophyll. Many of the *Florideæ* are almost green, and these grow near the surface; the deeper-growing ones increase in redness the deeper they occur. It is assumed that the red dye absorbs the dissolved oxygen of the water.

N. H. M.

### Physiological Meaning of the Cyanic Colouring Matters.

By L. KNY (*Bied. Centr.*, 1894, 23, 546—547; from *Naturw. Rundsch.*, 1893, 620).—According to Kerner, the object of the cyanic colouring matters is to protect the chlorophyll in young organs by shading from the light, or, on the underside of leaves, to convert light rays into heat rays. In stems and leaf veins, Pick and Kerner connect their presence as screens with the movement and decomposition of plastic substances.

An alcoholic chlorophyll solution was exposed to light which first passed through a red extract of *Beta vulgaris* (*var. rubra*), and through a white extract of *B. vulgaris* (*var. rapa*) respectively. It was found that the red solution did delay the decomposition of the chlorophyll, as the solution kept under the white extract was first changed.

As regards the transformation of light rays into heat by the colouring matters, it was found that when the leaves of beech, hazel, barberry, maple, cabbage, *Dracaena ferrea*, *Canina indica*, and beet, were exposed to sun light previously passed through alum solution, the temperature of the vessels containing red leaves became higher than in the case of green or white leaves. The greatest difference was 4°. When the direct light was cut off, the vessels containing the red leaves cooled first, the temperature of both vessels becoming about equal in 10 or 20 minutes.

N. H. M.

**Presence of Several Distinct Chlorophylls in the Same Vegetable Species.** By A. ÉTARD (*Compt. rend.*, 1894, 119, 289—291). See this vol., i, 66.

**Calcium Citrate in Plants.** By C. WEHMER (*Ann. Agm.*, 1894, 20, 391; from *Ber. deut. bot. Ges.*, 1893, 333).—After calling attention to the very sparing solubility of calcium citrate in water, the author suggests that some of the crystalline deposits in plants (such as the

raphides and some sphero-crystals), hitherto supposed to be calcium oxalate, may be citrate. Citric acid has a rôle in respiration; it is by no means demonstrated that all the carbonic anhydride liberated during respiration is produced from albumin, and it seems more likely that acids containing large amounts of oxygen may undergo complete combustion. N. H. M.

### **Nutrition of Plants by Humus and Organic Substances.**

By E. BRÉAL (*Ann. Agron.*, 1894, 20, 353—370).—A large portion of the paper is a *résumé* of experiments hitherto made on vegetation, without any organic matter, with humus substances and stable manure, water culture experiments with mineral salts and calcium humate, and experiments on the direct absorption of organic matter by plants. Although there was no doubt as to the beneficial effect of humus on plants, there was no evidence to show that the humus was directly absorbed, excluding the possibility of the intervention of lower organisms.

In the first experiment now described, a tuft of grass (*Poa annua*) was taken from the soil, the roots cut off and fresh roots obtained by water culture. The tuft was next divided into two equal parts, the one placed in a dish of potassium humate (carefully prepared from soil), whilst the roots of the other portion, after cutting off the tops, were placed in a similar vessel containing the same amount of potassium humate solution. In two or three days the roots of the whole plants entirely removed the potassium humate, the bottom of the dish being perfectly white; whilst the roots alone in the other dish seemed to have had no effect, the liquid being as dark as at first. On filtering the two liquids and estimating the carbon, the liquid which had contained the entire plants gave only 0.005 gram of carbonic anhydride, the other 0.025 gram. The potassium humate, had, therefore, been directly absorbed by the plants.

Other experiments are described confirming this result. The roots of *Poa* left in water over a filter paper covered with potassium humate, adhered tightly to the paper, leaving marks, when removed, resembling those which Sachs obtained by the corroding action of roots on marble. When trefoil plants and roots respectively were kept in solutions of sodium humate, the results obtained were similar to those with *Poa* and potassium humate.

Finally, an experiment is described in which the roots of entire plants (*Poa annua*), suspended in a solution containing sugar, completely absorbed the sugar, whilst the roots alone of similar plants did not. In this case, again, the absorption must have been direct, without the intervention of lower organisms. N. H. M.

**Agricultural Value of Various Natural Phosphates.** By G. PATUREL (*Ann. Agron.*, 1894, 20, 316—348).—The natural phosphates of various places, especially those of Brittany, have various commercial values attributed to them which do not always correspond with the effect produced by them on crops. The object of the present investigation was to ascertain why the phosphate of the green-stone (Boulonnais) are preferred to those of the Somme.



The employment of ammonium citrate or oxalate for the estimation of available phosphoric acid, does not give trustworthy results when applied to natural phosphates. Weak acids, such as acetic acid (Dehérain) or citric acid (Dyer), seem much more likely to give good results, as their action is comparable with both that of the acid of the soil and of root sap.

The results of the author's experiments on the action of dilute citric acid on the two phosphates in question, show, in the first place, that a 10 per cent. solution of citric acid dissolved very much more than a 1 per cent. solution. The amount of phosphates dissolved depended, however, on the amount of lime present when the results obtained with acid solution of a particular strength are compared. Thus, a Somme phosphate (with 24 per cent. total phosphoric acid and 13.8 per cent. of lime) gives up a smaller percentage of phosphoric acid than the Boulonnais phosphate (with 19 per cent. of total phosphoric acid and 7.6 per cent. of lime). Calcium carbonate seems to have a special retarding effect on the solvent action of the acid. This is not due merely to the neutralisation of the acid by the lime, as the differences in the amounts dissolved from the two phosphates were almost the same, whether 10, 5, 2, or 1 per cent. solutions were employed. In the case of a chalky phosphate (phosphoric acid 16.24, lime 57.2 per cent.), practically no phosphoric acid (less than 1 per cent.) was dissolved. In this case, the 1 and 2 per cent. acid solutions hardly showed an acid reaction after 24 hours.

The next experiments were made with acetic acid. Except that acetic acid is a much feebler solvent for the phosphate than is citric acid, the results were similar.

The effect of carbonic anhydride alone, in conjunction with citric acid, and with acetic acid respectively, was also examined. Carbonic anhydride alone dissolved very little of the phosphate, and did not have any marked effect when employed with acetic or citric acid. In a subsequent experiment, however, in which the phosphates had been kept for some time in water containing carbonic anhydride, then extracted with 10 per cent. acetic acid solution, a considerably higher percentage of phosphoric acid was dissolved, doubtless because a part of the lime had been dissolved by the carbonic anhydride.

The results of the experiments showing that the Boulonnais phosphate was more soluble in citric acid than the Somme phosphate is in accordance with the known effect of the two manures in agriculture.

In estimating the value of mineral phosphates, the quantity of lime as well as that of phosphoric acid (soluble in dilute acid) should be determined. In the case of such phosphates as those of the Somme, it would probably be worth while to remove part of the lime before applying them to the land. This is, however, a point to be decided by direct field experiments.

N. H. M.

## Analytical Chemistry.

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**Iodometric Estimation of Telluric acid.** By F. A. GOOCH and J. HOWLAND (*Zeit. anorg. Chem.*, 1894, **7**, 132—136).—Telluric acid is reduced by hydriodic acid, and iodine is set free; but when the free iodine is titrated with sodium thiosulphate, from 20—26 per cent., more iodine is found than that required for the reduction to tellurous acid. Telluric acid may be accurately estimated as follows. The telluric acid is treated with potassium bromide and dilute sulphuric acid in a distillation apparatus, and a stream of carbonic anhydride passed through the boiling solution in order to remove the bromine. The latter is conducted into a solution of potassium iodide and the liquid titrated with sodium thiosulphate. The results agree very well with one another and with the acceptance of 127 as the atomic weight of tellurium.

The authors prepare their standard solution of tellurium as follows. Tellurium dioxide, obtained by dissolving pure tellurium in nitric acid and heating the product at a red heat, is dissolved in strong potassium hydroxide and precipitated with dilute sulphuric acid. The precipitate is dissolved in sulphuric acid (diluted one half), treated with excess of potassium permanganate, neutralised with oxalic acid, and the excess of oxalic acid carefully destroyed with dilute permanganate solution.

A series of twelve determinations of the equivalent weight of tellurium dioxide by Brauner's method (*Trans.*, 1891, 258), gave the molecular weight of tellurium dioxide = 159, and the atomic weight of tellurium = 127 (O = 16).  
E. C. R.

**Volumetric Estimation of Phosphorus in Steel.** By W. A. NOYES and E. D. FROHMAN (*J. Amer. Chem. Soc.*, 1894, **16**, 553—559).—The method proposed by Dudley and Pease (*Abstr.*, 1893, ii, 553) is rapid and easy of execution and gives concordant results. There is, however, an uncertainty of about 10 per cent. as regards the factor which should be used for converting the iron equivalent of the permanganate solution into the phosphorus equivalent. The author's experiments conclusively prove that if the reduction of the molybdate compound by means of zinc and sulphuric acid is properly executed the metal exists in a form corresponding with the oxide  $\text{Mo}_2\text{O}_3$ . The conditions are (i) that the passage of the solution through the reducing flask should be preceded by that of some dilute acid, so that most of the air in the reducing flask may be expelled before the solution enters it; (ii) that the diluted solution shall pass through the reducing flask slowly and be followed by the acid wash-water without allowing any air to enter at the top; and (iii) that the reduced solution shall be titrated at once and without further dilution. It should be of a pure green, not an olive-green colour.

It is now a thoroughly established fact that in the yellow ammonium phospho-molybdate there exist twelve molecules of molybdic anhydride to one atom of phosphorus. The quantity of the latter may

therefore be very correctly calculated from the amount of permanganate required to reoxidise the  $\text{Mo}_2\text{O}_3$  to  $2\text{MoO}_3$ . L. DE K.

### Analysis of an Apatite in a Laminated Graphite from Ceylon.

By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, 1894, 7, 154—157).—The analysis was conducted as follows:—About 0.5 gram of the mineral is dissolved in strong nitric acid and evaporated to dryness with mercuric oxide. The residue is moistened with nitric acid, dissolved in water, heated to boiling, and neutralised with ammonia, whereby the phosphoric acid is precipitated as mercuric and calcium phosphates. The precipitate is washed, heated over a bare flame, dissolved in dilute nitric acid, and precipitated with molybdenum solution. The filtrate is concentrated, the excess of molybdic acid filtered off and the remainder of the molybdenum precipitated as sulphide; the iron and aluminium are then estimated in the solution. The filtrate from the iron and aluminium contains manganese, magnesium and calcium; these are separated by a method previously described (*Zeit. anorg. Chem.*, 6, 57). The filtrate from the mercuric and calcium phosphates contains a small quantity of calcium and the alkalis. It is evaporated to dryness, heated until the mercuric oxide is separated, and then dissolved in hydrochloric acid; the calcium is determined as oxalate, the potassium by platinic chloride, and the sodium weighed as sulphate.

The chlorine in the apatite is determined by dissolving a portion in nitric acid containing silver nitrate: the fluorine by heating with concentrated sulphuric acid in a platinum apparatus and collecting the hydrogen fluoride evolved in pure sodium hydroxide and precipitating as calcium fluoride. E. C. R.

### Detection and Estimation of Small Quantities of Arsenic in Copper.

By F. A. GOOCH and H. P. MOSELEY (*Zeit. anorg. Chem.*, 1894, 7, 127—131).—The estimation is based on a method described by Sanger (*Abstr.*, 1892, 382), whereby the mirror of arsenic obtained is compared with a series of standard mirrors. Not more than 1 gram of the copper is dissolved in dilute nitric acid, 2—3 c.c. of strong sulphuric acid is added and the solution evaporated until fumes of sulphuric acid are evolved. The concentrated residue is then distilled with strong, hydrochloric acid and potassium bromide, and the distillate collected in dilute hydrochloric acid. The distillate is again distilled with a fresh quantity of potassium bromide, and the final distillate is treated with a small quantity of stannous chloride dissolved in hydrochloric acid in order to convert any free bromine into hydrobromic acid; it is now ready for the Marsh's apparatus. The results obtained by the authors show that 0.05 milligram of arsenic may be determined by this process with fair accuracy; and they give the results of analyses of commercial copper containing from 0.01—0.0005 per cent. of arsenic. E. C. R.

**Apparatus for the Estimation of Carbonic Anhydride.** By A. C. CHRISTOMANOS (*Ber.*, 1894, 27, 2748—2751).—The apparatus described by the author is a modification of Bunsen's well-known appa-

rtus, sulphuric acid being substituted for calcium chloride as the drying agent, and a more stable form given to the whole.

A. H.

**Estimation of Carbonic Anhydride in the Air.** By F. KRAT-SCHMER and E. WIENER (*Monatsh.*, 1894, 15, 429—432).—The method described in this paper depends on the fact that when a solution of sodium carbonate is titrated with sulphuric acid at the ordinary temperature, using phenolphthaleïn as indicator, decolorisation of the latter takes place as soon as one-half of the sodium carbonate has been decomposed with formation of sodium sulphate and sodium hydrogen carbonate. With a mixture of solutions of sodium hydroxide and carbonate, decolorisation takes place as soon as the whole of the former and half of the latter have been neutralised. If, therefore, equal volumes of a solution of sodium hydroxide be titrated with sulphuric acid, the one immediately, and the other after shaking with a known volume of air containing carbonic anhydride, the difference in the amount of acid required in the two cases is equivalent to one-half of the amount of sodium carbonate formed by the carbonic anhydride.

The authors employ a solution of sulphuric acid of such strength that 1 c.c. is equivalent to 1 milli gram of carbonic anhydride, and the number of milligrams of carbonic anhydride in any volume of air taken is found by doubling the number of cubic centimetres representing the difference between the two titrations.

H. G. C.

**Indirect Methods of Analysis.** By H. SCHIFF (*Gazzetta*, 1894, 24, ii, 30—36).—In connection with the work of Forte (Abstr., 1894, ii, 332), the author refers to his own papers (*Annalen*, 105, 219; 107, 69) on indirect methods of analysis.

W. J. P.

**Avoidance of Certain Causes of Error in Hydrotometric Analysis.** By A. BOMBOLETTI (*Gazzetta*, 1894, 24, ii, 26—30).—On applying Clark's soap test to very hard waters, running the soap solution into the undiluted sample, and also into diluted portions, the results obtained are not concordant among themselves. If the water is rich in earthy matter, it should be diluted with distilled water until the hardness is about 22° (parts of calcium carbonate per 100,000 parts of water). If the water is soft, the results obtained by the soap test make it seem too hard. In this case, the standard solution of calcium chloride, whose hardness is known, is diluted until of about the same degree of hardness as that of the sample under examination; the hardness of this is then determined and is found to be greater than the extent of the dilution indicates. Taking the degree of dilution of the standard into consideration, the true hardness of the water to be examined can be calculated (compare Neugebauer, Abstr., 1891, 116).

W. J. P.

## General and Physical Chemistry.

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### **Refractive Indices of Aqueous Solutions of Cadmium Salts.**

By R. DE MUYNCK (*Ann. Phys. Chem.*, 1894, [2], 53, 559—563).—From a study of the transference of the ions in solutions of cadmium salts, Hittorf (1859) was led to the conclusion that these solutions contain double, or even triple, molecules of the salts in question. The author has, with the aid of the Pulfrich refractometer, determined the refractive indices of solutions of several cadmium salts, in order to ascertain whether the optical properties of these solutions indicate any peculiarities in the molecular condition of the dissolved salts. No abnormal results were, however, obtained, a careful comparison with zinc iodide and similar salts showing that with reference to the refractive indices, the behaviour of solutions of cadmium salts is normal.

H. C.

### **Refractometric Observations.** By J. F. EIJKMAN (*Rec. Trav.*

*Chim.*, 1894, 13, 13—33).—The author describes the apparatus and methods employed in his refractometric researches. (See *Abstr.*, 1893, ii, 1.)

H. C.

**Spectrum of the Electric Discharge in Liquid Oxygen, Air, and Nitrogen.**—By G. D. LIVEING, and J. DEWAR (*Phil. Mag.*, 1894, [5], 38, 235—240).—Liquid oxygen, air, and nitrogen, like non-electrolysable compound liquids, offer great resistance to the passage of an electric discharge, so that the spark could only be made to pass through a thickness of 1 mm. of liquid. When the thickness was less than this, a succession of sparks could be maintained; but the resistance appeared to be very great, and the disruptive effect on the platinum electrodes was sufficient to discolour the liquid by the particles thrown off their surfaces. The discharge through the liquid in all cases gave a continuous spectrum and some bright lines traceable to the electrodes, whilst the rays supposed to have been emitted by the molecules of the liquid were less conspicuous. It seems not unlikely, therefore, that the continuous spectrum was due to the particles thrown off the electrodes.

With liquid oxygen boiling at atmospheric pressure, and both electrodes being immersed in the liquid at a distance of 1 mm. or less, a continuous spectrum is obtained, brightest in the yellowish-green, but extending to some distance both on the red and on the blue side. The absorption bands of oxygen were conspicuous on this bright background. With a Leyden jar in circuit, the brilliance of the spectrum is increased and some additional lines brought out. Many more bright lines were produced by keeping only the lower electrode immersed in the liquid, so that the spark passes partly through the liquid and partly through the gas immediately above it. Most of these correspond with known lines of oxygen. Exhaustion of the gas above the liquid, until the pressure was reduced to about 10 mm.

of mercury, did not make any marked difference in the appearance of the spectrum so long as both electrodes were immersed in the liquid. But when the lower electrode only was immersed and a Leyden jar put in circuit, a good many bright lines came out. One of these is a line of wave length about 557, and may be identical with the auroral line, but further experiments will be required before the identity can be regarded as proved.

The passage of the discharge through the liquid produced much ozone. Not only was the smell of ozone very strong, but the liquid took the indigo tint, deeper than the blue of ordinary oxygen, which is characteristic of ozone. On one occasion, after the sparks had been passed through the liquid for a short time, an explosion ensued which shattered the vessel. This may have been an explosion of ozone.

The effects of the discharge through liquid air were very similar to those produced with liquid oxygen, as long as the pressure was that of the atmosphere, and no jar was in circuit. When a jar was used a much larger number of lines, generally resembling the ordinary air lines, were seen but not measured. When the pressure was reduced, the usual banded spectrum of nitrogen was seen, and was strong relatively to the spectrum of oxygen. As the liquid evaporated, and thereby lost more nitrogen than oxygen, the two green bands due to oxygen appeared to become stronger actually, as well as relatively to the nitrogen bands. In this case, the discharge produced oxides of nitrogen, which were detected in the residual gas when the air had all evaporated.

With liquid nitrogen at atmospheric pressure, both electrodes immersed, a faint very diffuse line was observed at about  $\lambda 501$ . This became more distinct when only one electrode was immersed, and probably represents the strong double line of nitrogen in that position. With the jar in circuit, the spectrum was a series of bright lines similar to those given by gaseous nitrogen at atmospheric pressure. Under reduced pressure, one or both electrodes being immersed, and no jar used, the band spectrum of nitrogen appeared. On putting on the jar, this was replaced mainly by the line spectrum.

The spark spectrum of distilled water at the ordinary temperature and pressure was examined for the sake of comparison. Only hydrogen lines were obtained and none that could be identified with those of oxygen.

H. C.

**Clark Cell when producing a Current.** By S. SKINNER (*Phil. Mag.*, 1894, [5], 38, 271—279).—The experiments detailed in this paper were made with the object of ascertaining how far the total E.M.F. round the circuit differs from that of the open cell, in the case of a Clark cell which is being used to produce a current, and how far this new value for the E.M.F. changes when the current is maintained. The experiments were made on three cells, all much larger than the ordinary Board of Trade pattern of Clark cell. It was assumed that the total E.M.F. round the circuit is equal to that of the cell at rest; and therefore that the E.M.F. overcoming polarisation can be obtained by subtracting from the E.M.F. of the cells at rest the observed current. In this way it was found that

1. The E.M.F. of polarisation varies directly with the current density in a particular cell.

2. The E.M.F. of polarisation slowly increases when the current is maintained.

From the magnitudes of the quantities found in the experiments, it follows that small currents of approximately known value can be obtained by the use of Clark cells of small internal resistance which may be neglected in comparison with the large external resistance.

H. C.

**Magnesium Voltaic Cell.** By H. N. WARREN (*Chem. News*, 1894, 70, 179).—Attention is drawn to a modified Daniell cell with magnesium immersed in a strong solution of ammonium chloride in the porous pot, and a strongly acid saturated solution of cupric chloride in the outer receptacle.

D. A. L.

**Potential Differences between Metals and Electrolytes.** By V. ROTHMUND (*Zeit. physikal. Chem.*, 1894, 15, 1—32).—A capillary tube containing mercury or a liquid amalgam dips into a small cup containing mercury, covered by the electrolyte, and the capillary and electrolyte can be brought to any required difference of potential by means of a set of resistance coils and a Leclanché cell. The capillary tube is connected with a manometer, and the mercury always brought to the same point by an increase or decrease of the manometric pressure. When the E.M.F. due to the cell is equal to that between the amalgam and electrolyte no charge is received, and the surface tension is a maximum; the method hence consists in varying the difference of potential due to the cell until the manometric pressure required to bring the amalgam to its constant point reaches a maximum. Measurements were made with mercury and amalgams of lead, bismuth, tin, copper, zinc, and thallium, the electrolytes being sulphuric acid saturated with a salt of the dissolved metal, and with a complex mercury salt, such as mercuric potassic iodide. The E.M.F. of various galvanic chains were calculated from the results and compared with those obtained by direct measurement. The agreement was in most cases very satisfactory, so that the potential difference between the two metals or two electrolytes has but a slight influence on the E.M.F. of the cell. Variations occurring in the cases of the amalgams of tin, cadmium and thallium are probably due to the action of the acid on the surface of the amalgam. Discordant results were also obtained in the experiments with the complex salts, where it is noticeable that the absolute value of the surface tension at the maximum was below the normal value, in which case the author does not consider the method to be applicable.

L. M. J.

**Determination of the Resistance of Electrolytes.** By F. KOHLRAUSCH (*Zeit. physikal. Chem.*, 1894, 15, 126—130).—A criticism of the method employed by Wildermann (*Abstr.*, 1894, ii, 376). The author is of opinion that the telephone method with alternate currents can be employed for much higher resistances than those examined by

Wildermann, and is more convenient and simple than the method of the latter, which involves the use of strong batteries. In the cases of much higher resistances, 100,000 ohms and more, he does not consider Wildermann's method sufficiently accurate to render its application useful.

L. M. J.

**Electrolytic Dissociation.** By S. TANATAR (*Zeit. physikal. Chem.*, 1894, 15, 117—123).—The decrease of conductivity of salts by the addition of alcohol is ascribed not to a decrease in the dissociation but to the increase of the ion friction. Addition of alcohol, however, also caused a decrease in the inversion velocity of sugar by salts, although this is dependent on the dissociation only. The author, therefore, attempts to estimate, by means of the thermal effects, the dissociation changes caused by alcoholic dilution. In all cases the thermal effects due to the water alone are observed simultaneously, and allowed for in the results. The addition of a 2N solution of hydrochloric acid to an equal volume of alcohol produces a heat absorption of only 0.137 Cal., so that the 2N solution in water and the 1.03N solution in 44 per cent. alcohol appear to be approximately equally dissociated. The addition of 300 c.c. alcohol to 250 c.c. of a 2N solution produced a development of about 1.02 Cal., apparently indicating increased dissociation. Potassium chloride dissolved in alcohol gives rise to a greater heat absorption than in water, the quantity being determined, both indirectly and directly, with concordant results. This effect is not an exceptional one, the same result obtaining with alcoholic solutions of potassium nitrate, sodium chloride, cane-sugar, acetic acid, and methylic alcohol, whilst it is also noticeable that the freezing point depression with potassium chloride is greater in dilute alcoholic than in aqueous solution.

L. M. J.

**Melting Point Determinations at a Red Heat.** By V. MEYER, W. RIDDLE, and T. LAMB (*Ber.*, 1894, 27, 3129—3143; compare *Abstr.*, 1894, ii, 6 and 268).—In place of the method already described (*loc. cit.*), it is found advantageous to determine the melting point of a small quantity of the salt contained in a platinum tube which is secured to the air-thermometer employed. A thick piece of platinum attached to a fine wire is dipped into the molten salt, which is then allowed to solidify; the wire, passing over a pulley, suspends a weight, which, in falling, strikes a bell. When fusion occurs, the weight is released, indicating the moment at which to observe the temperature.

The following melting points have been determined. Sodium chloride, 815°; sodium bromide, 757°; sodium iodide, 661°; potassium chloride, 800°; potassium bromide, 722°; potassium iodide, 684°; sodium carbonate, 849°; potassium carbonate, 878°; sodium sulphate, 863°; potassium sulphate, 1078°; rubidium iodide, 641°; caesium iodide, 621°; calcium chloride, 806°; strontium chloride, 832°; barium chloride, 921°.

M. O. F.

**Melting Points of Mixtures of Isomorphous Salts.** By F. W. KÜSTER (*Zeit. physikal. Chem.*, 1894, 15, 86—88).—The author



points out that in Le Chatelier's researches on the melting points of isomorphous mixtures, out of the seven pairs of salts employed only three pairs are truly isomorphous, namely, (1) the carbonate and sulphate of potassium, (2) the similar salts of sodium, (3) the sulphate and chromate of potassium. The method also is only approximate, whilst the number of points taken is insufficient for an accurate construction of curves; on this account the author is of the opinion that there is no experimental ground for supposing that the melting point curves of mixtures of salts depart more from straight lines than those of other compounds (see *Abstr.*, 1894, ii, 179).

L. M. J.

**Law of Corresponding Boiling Points.** By U. DÜHRING (*Ann. Phys. Chem.*, 1894, [2], 52, 556—588).—The law of corresponding boiling points was enunciated by the author in 1877, and can be formulated thus—

$$(t' - s')/(t - s) = q = \text{const.},$$

or

$$t' = s' + q(t - s),$$

where  $s$  and  $t$  are the boiling points of a substance at the pressures  $p_1$  and  $p_2$ , and  $s'$  and  $t'$  are the equivalent boiling points of some other substance. This law is attributed by Young to Colot (*Phil. Mag.*, 1892, [5], 34, 510), in a paper in which Young maintains that this formula is only an approximation, and does not represent the facts as closely as the formulæ proposed by Ramsay and Young. The author in this paper quotes a large number of experimental results which are in better accordance with his law than with that which Young defends.

H. C.

**Dühring's Law of Corresponding Boiling Points.** By G. W. A. KAHLBAUM and C. G. V. WIRKNER (*Ber.*, 1894, 27, 1894—1902).—The authors apply Dühring's formula (preceding abstract) to Kahlbaum's experimental results (*Ber.*, 27, 1386), and find only an approximate agreement between the calculated and observed values, the differences being far greater than the probable errors of experiment.

H. C.

**Law of Corresponding Boiling Points.** By U. DÜHRING (*Ber.*, 1894, 27, 3028—3035).—A reply to Kahlbaum and Wirkner (see preceding abstract).

H. C.

**Fluidity of Metals at Temperatures Below their Melting Points.** By W. SPRING (*Zeit. physikal. Chem.*, 1894, 15, 65—78).—Many metals, when heated to temperatures considerably below their melting points, exhibit properties characteristic of the liquid state. For examination in this respect, the metals were turned into cylinders with ends as perfectly plane as possible, and placed end to end in an iron holder, pressure being applied by a screw. They were heated in this condition in a hot air bath, filled, if necessary, with an indifferent gas. Cylinders of aluminium, bismuth, cadmium, copper, tin, gold, lead, zinc, antimony, and platinum were employed, and in the first experiment two cylinders of the same metal were used. The tempera-

ture was kept for from 4 to 8 hours at from 200° to 400°, and it was found that, except in the case of antimony and platinum, the cylinders had alloyed so perfectly that they could be turned with one end fixed in a lathe, whilst if broken in a vice the fracture did not take place along the original surface of separation. Pairs of different metals were next employed, usually copper or lead with some of the other metals, with the result that, at the junction, an alloy of considerable thickness was formed, 18 mm. in the case of zinc and copper, and 15 mm. in the case of cadmium and copper. In the case of lead and tin, a cavity in the end of one metal was filled with mica, so that contact only took place at the edge. An alloy was formed to the thickness of 15 mm., of which 9 mm. were in the tin and 6 mm. in the lead. By the use of cylinders of copper and zinc, in which, owing to a central cavity, contact only took place at the edges, it was found that the surface of the copper above the cavity was coloured by a yellow alloy resembling that formed when copper is subjected to the action of zinc vapour, and which was not due to diffusion from the edges (see also Abstracts, 1893, ii, 168). For the explanation of these results, which are most marked with soft and non-crystalline metals, the author points out the assumption suffices, that the molecules of solids, like those of fluids, do not all move with the same velocity.

L. M. J.

**Pressure, Volume, and Temperature Relations of Rarefied Gases.** By E. C. C. BALY and W. RAMSAY (*Phil. Mag.*, 1894, [5], 38, 301—327).—After a summary of previous work on the subject of the volume and thermal expansion of gases under reduced pressure, the authors give a description of their apparatus, which consisted essentially of two McLeod gauges placed side by side, and connected on the one hand with a mercury pump for exhausting them, and on the other with apparatus for the admission of measured quantities of the gas under examination. On testing the McLeod gauges, the authors found that whilst they gave good results with pure hydrogen at high vacua, they were absolutely untrustworthy with carbonic anhydride under the same conditions, owing to surface condensation on the glass.

By heating one of the gauges to a known temperature by means of a vapour jacket, and comparing its readings with those of the other gauge, the following values were obtained for the coefficient of expansion of hydrogen.

Pressure in mm.....	4.7	3.47	0.25	0.096	0.077
Coeff. of expansion..	1/273.5	1/273.7	1/276	1/297	1/300.5

The coefficient of expansion of oxygen varied as follows.

Pressure in mm.....	5.1	2.5	1.4	0.083	0.07
Coefficient of expansion..	1/261	1/251	1/233	1/244	1/240

For nitrogen the numbers obtained were

Pressure in mm.....	5.3	3	1.1	0.8	0.6
Coefficient of expansion..	1/304	1/302	1/304	1/331	1/343

It was found that at a pressure of about 0·7 mm. the behaviour of oxygen was very abnormal, no definite readings being obtainable, and the coefficient of expansion sinking as low as 1/1500. This confirms Bohr's observation of the abnormality of oxygen with respect to Boyle's Law at a pressure of 0·7 mm. J. W.

**Adsorption.** By G. C. SCHMIDT (*Zeit. physikal. Chem.*, 1894, **15**, 56—64).—As the adsorption of gases by porous substances, such as charcoal, has been shown to obey Henry's Law, experiments were made with dilute solutions. Animal charcoal placed in iodine solution was first examined, and the ratio  $C_2/C_1$  obtained, where  $C_2$  is the quantity of iodine adsorbed by the charcoal, and  $C_1$  the concentration of the iodine solution. This ratio is not constant, but an approximate constancy obtains for the ratio  $C_2^4/C_1$ . Experiments were similarly made with charcoal and acetic acid, the concentration being calculated for undissociated acid, also with cellulose and picric acid, and with silk and eosin or malachite green, but in no case was Henry's law obeyed. The author then contests the view that the process of dyeing consists in the formation of a solid solution, as, were it so, the partition coefficient between the solution and material dyed should be constant; but this his experiments with silk showed was not the case. That in true solid solution the partition coefficient is constant, is indicated by experiments with silicic acid and various solutions, the results in the cases of the sulphates, chlorides, and nitrates of potassium and hydrogen showing excellent agreement. From this, it is concluded that dyeing is not a case of solution, but is due to a surface action, and is akin to adsorption. L. M. J.

**Passage of Hydrogen through a Palladium Septum.** By W. RAMSAY (*Phil. Mag.*, 1894, [5], **38**, 206—218).—As palladium at moderately high temperatures permits hydrogen to pass through it, but not other gases, it behaves as a semipermeable membrane for mixtures of hydrogen with other gases. The author has made experiments to determine whether the pressures of hydrogen within and without a vessel of palladium become identical when the vessel is previously filled with nitrogen or another gas, and the hydrogen is allowed to pass inward through the walls. The following table shows the results obtained with different gases, the numbers being the ratio of the pressure of hydrogen inside the vessel to that outside the vessel after equilibrium had been reached.

Ratio from hydrogen and nitrogen at 280° .....	0·905
Ratio at 335° .....	0·898
Ratio with 50 per cent. of hydrogen at 335° .....	0·936
Ratio with 25 per cent. of hydrogen at 335° .....	0·934
Ratio from hydrogen and carbonic anhydride at 280° ...	0·962
Ratio from hydrogen and carbonic oxide at 280° .....	0·954
Ratio from hydrogen and cyanogen at 280° .....	0·969

The numbers approximate to the "theoretical" ratio 1, but never reach it. The author discusses the mechanism of the passage of

hydrogen through palladium, and is disposed to the opinion that the hydrogen during its passage is in the atomic state. J. W.

**Molecular Surface Energy of Ethereal Salts.** By W. RAMSAY and Miss E. ASTON (*Proc. Roy. Soc.*, 1894, **56**, 162—170; and *Zeit. physikal. Chem.*, 1894, **15**, 98—105).—The ethereal salts studied by Young with reference to their thermal properties were subjected by the authors to an investigation of their surface energy. The following table contains the values of the constants  $k$  and  $d$  in the equation  $\gamma(Mv)^{\frac{1}{3}} = k(\tau - d)$ .

	Critical temp.	$k$ .	$d$ .
Methylic formate .....	214.0°	2.042	5.9
„ acetate.....	233.7	2.109	4.5
„ propionate.....	257.4	2.182	5.3
„ butyrate.....	281.25	2.220	3.75
„ isobutyrate ....	267.55	2.248	5.25
Ethylic formate .....	235.4	2.020	4.5
„ acetate .....	251.0	2.226	6.7
„ propionate.....	272.9	2.240	4.9
Propylic formate .....	264.85	2.110	4.85
„ acetate .....	276.2	2.227	5.0

It is apparent that the value of the constant  $k$  increases with the molecular weight, but never differs greatly from the mean value 2.121 for non-associating liquids. J. W.

**Molecular Surface Energy of Mixtures of Non-associating Liquids.** By W. RAMSAY and Miss E. ASTON (*Proc. Roy. Soc.*, 1894, **56**, 182—191; and *Zeit. physikal. Chem.*, 1894, **15**, 89—97).—The authors have investigated the change of capillarity with temperature in the following mixtures:—Toluene and piperidine, benzene and carbon tetrachloride, chlorobenzene and ethylenic dibromide, and chloroform and carbon bisulphide. The method was that of Ramsay and Shields. All the above liquids show no associating tendency when pure, and it was found that whilst the capillary rise, and the surface tension might differ from the average value when they were mixed, the rate of change of the molecular surface energy with the temperature remained normal, so that the average molecular weight of the mixture could be calculated. In the case of the mixture of chloroform and carbon bisulphide, there appears to be slight association at low temperatures. J. W.

**Complexity and Dissociation of Liquid Molecules.** By W. RAMSAY (*Proc. Roy. Soc.*, 1894, **56**, 171—182; and *Zeit. physikal. Chem.*, 1894, **15**, 106—116).—The author summarises the facts which have been held by Guye and others to indicate molecular complexity in liquids such as water, the alcohols, and the organic acids. From determinations of the molecular surface energy of these liquids at various temperatures, it is possible to calculate the degree of this complexity by means of the formula

$$x = \left( \frac{2.121 (1 + \mu\tau)}{k} \right)^{\frac{1}{3}},$$

where  $\alpha$  is the complexity factor, and  $\mu$  a constant for each substance. The following table contains the values of  $\alpha$  for different temperatures.

Temperatures ....	20°.	40°.	60°.	80°.	100°.
Methylic alcohol..	2.32	—	—	2.14	2.09
Ethylic alcohol ...	1.65	1.59	1.52	1.46	1.39
Water .....	1.64	1.58	1.52	1.46	1.40
Acetic acid .....	2.13	2.06	1.99	1.92	1.86

J. W.

**Relation between the Surface Tension and Osmotic Pressure of Solutions.** By B. MOORE (*Phil. Mag.*, 1894, [5], 38, 279—284).—An attempt to show that osmotic pressure may be produced by difference in surface tension acting along the exceedingly fine capillary openings of almost molecular dimensions, which place the solution in connection with its solvent in the pores of the semipermeable wall which separates them.

H. C.

**Cryoscopic Molecular Weight Determinations.** By K. AUWERS (*Zeit. physikal. Chem.*, 1894, 15, 33—55).—Hydroxy-compounds, except phenols, when examined in solution in benzene, if the solutions are not too dilute, usually give abnormal values for the freezing point depression, whilst normal values are obtained with the ketones and aldehydes. The author, therefore, makes a large number of determinations of the lowering of the freezing point of this solvent by a number of oxy-compounds, and from the results in some cases, discusses the probable constitution of the compounds.

Over 80 compounds were examined; chiefly keto-acids, keto-aldehydes, and the acidic derivatives of primary and secondary organic bases. Normal values are obtained with the derivatives of acetoacetic acid, and diacetylacetone appears also to be an entirely ketonic compound.

Similar results are obtained with the oxymethylene ketones, whilst allylic alcohol gives very abnormal values, thus differing from those compounds in which the hydroxyl-group is united to the doubly-linked carbon atom. The acid derivatives of primary bases also give abnormal results, but the variations disappear in the secondary and tertiary compounds, this being explained by the supposition of the migration of the imidic hydrogen. The mercaptans differ from the alcohols, being cryoscopically normal, whilst dithienyl,  $C_8H_6S_2$ , gives a normal value, although thiophen itself gives an abnormally high result.

L. M. J.

**Freezing-Point Depressions in Dilute Alcoholic Solution.** By S. TANATAR, J. CHOINA, and D. KOZIREFF (*Zeit. physikal. Chem.*, 1894, 15, 124—125).—The freezing-point depressions in mixtures of water and methylic or ethylic alcohol are observed for acetic acid, ethylic or methylic alcohol, sodic chloride, potassic chloride, hydrogen chloride, potassium nitrate, and cane-sugar. The depressions produced by the non-dissociated compounds, acetic acid and the alcohols, differ but little from those in pure water, that due to cane-sugar is

double the normal value, being equal to that due to the dissociated compounds. The salts, in all cases, give a greater depression than in pure water, the value increasing with the alcohol content.

L. M. J.

**Influence of Low Temperatures on the Laws of Crystallisation.** By R. PICTET (*Compt. rend.*, 1894, 119, 554—557).—All substances cooled below  $70^{\circ}$  become diathermanous, this characteristic becoming the more marked the lower the temperature to which they are cooled. In this behaviour, there is an explanation for the fact that a temperature of  $-68.5^{\circ}$  may be observed in liquid chloroform from which crystals are separating at  $-83^{\circ}$ , and when the temperature of the surroundings is  $-120^{\circ}$  to  $-130^{\circ}$ . To obtain the true temperature of crystallisation below  $-50^{\circ}$ , it is necessary to avoid supercooling, and to allow the crystallisation to take place very gradually.

H. C.

**Principle of Maximum Work and Entropy.** By BERTHELOT (*Compt. rend.*, 1894, 118, 1378—1392).—The author restates his well-known principle of maximum work. All apparent exceptions to this principle are explained as caused by the development or absorption of heat during the action, which is not of a purely chemical origin or character. The principle would hold in strictest form for reactions between solid substances at the absolute zero, the temperature being maintained constant, and the products of the reaction being also solid. If Kopp's law for the specific heats of solid substances were absolutely correct, the heat of the reaction would be independent of the temperature for solid substances, and the principle of maximum work would hold for temperatures other than the absolute zero.

According to known thermodynamical laws, when any system passes from the state  $a$  to the state  $b$  at constant temperature, the heat  $K$  developed during the change is always greater than the product of the absolute temperature  $T$  by the loss of entropy  $(S_a - S_b)$ ,

$$K > T(S_a - S_b).$$

If  $T$  or  $S_a - S_b$  are so small as to be negligible quantities,  $K > 0$ , a statement that is obviously in agreement with the principle of maximum work as already explained.

If the change in the value of  $S_a - S_b$  with  $T$  is a perfectly regular one, the relationship between the values of  $K$  for various systems at the absolute zero will hold at other temperatures. From this it would follow that the heat developed during chemical change at any given temperature may be considered as made up of two different portions, the one consisting in the heat that would be developed during the occurrence of the same change at absolute zero, and the other in the increase which is due to the raising of the temperature, a quantity that is evidently intimately related to the gain in entropy of the system. By calculation, this view is shown to be consistent with the results obtained for the displacement of bromine and iodine from bromides and iodides in solid form by solid chlorine at the absolute zero and at  $200^{\circ}$  C., and also for the displacement of iodine by bromine under like conditions.

H. C.

**The Assumption of a Special Nascent State.** By L. ANDREWS (*Chem. News*, 1894, **70**, 152—153).—It is asserted that the assumption that nascent hydrogen has a special activity is not necessary for the explanation of the reduction of ferric to ferrous chloride by zinc, of copper sulphate by zinc, of sulphuric acid by copper, or of nitric acid by various metals, as all may be regarded as cases of direct oxidation. D. A. L.

**Nascent State.** By J. C. GREGORY (*Chem. News*, 1894, **70**, 188—189).—The author does not consider the statements made in the preceding abstract have been positively demonstrated, and points out that there are many other instances of nascent activity that cannot be explained in the manner suggested; for instance, the activity of oxygen freshly liberated from ozone or set free from water by chlorine. D. A. L.

**Extraction Apparatus.** By L. ÉTAIX (*Bull. Soc. Chim.*, 1894, [3], **11**, 259—260).—The essential feature of this apparatus is a syphon tube, the short arm of which opens at the bottom of the extraction vessel, the long arm into the lower flask, the syphon being protected by an outer tube. By this means, the solvent used alternately half fills the extraction vessel, so as to cover the substance to be extracted, and is then automatically drawn off into the lower vessel. It may be used for cold or boiling extractions. L. T. T.

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## Inorganic Chemistry.

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**Action of Thionyl Chloride on Inorganic and Organic Acids and Aldoximes.** By C. MOUREU (*Compt. rend.*, 1894, 119, 337—340).—When pure sulphuric acid is mixed with excess of thionyl chloride, a mixture of sulphurous anhydride and hydrogen chloride, in molecular proportion, is evolved without appreciable development of heat, and the residue is a mixture of chlorosulphonic acid,  $\text{SO}_2\text{Cl}\cdot\text{OH}$ , and pyrosulphuric chloride,  $\text{S}_2\text{O}_5\text{Cl}_2$ .

With nitric acid, thionyl chloride acts violently, with development of heat and formation of nitroxyl chloride, sulphurous anhydride, and hydrogen chloride. Nitrogen oxides and sulphuric acid are also formed, in consequence of secondary actions between the hydrogen chloride, the excess of nitric acid, and the sulphurous anhydride.

Phosphoric, metaphosphoric, and boric acids are at once attacked by thionyl chloride, but with metaphosphoric acid the action is incomplete, whilst phosphoric and boric acids form chlorinated condensation products, which are not further attacked by the thionyl chloride.

Thionyl chloride, even at its boiling point, has no action on oxalic acid, but sodium, mercury, and silver oxalates yield a metallic chloride, sulphurous anhydride, and carbonic oxide and carbonic anhydride.



In order to moderate the action, the thionyl chloride must be dissolved in ether or benzene. No trace of oxalic chloride,  $C_2O_2Cl_2$ , was formed.

Anhydrous formic acid yields carbonic oxide, hydrogen chloride, and sulphurous anhydride, no liquid being left when the action is complete.

Aldoximes are violently attacked by thionyl chloride, but in presence of benzene the action proceeds regularly. The thionyl chloride acts as a dehydrating agent, and converts the aldoximes into the corresponding nitriles,  $R\cdot CH: NOH + SOCl_2 = SO_2 + 2HCl + R\cdot CN$ . With benzaldoxime the yield of nitrile is 70 per cent., with isovaleraldoxime 48 per cent., and with cœnanthaldoxime 62 per cent.

C. H. B.

**Secondary Products containing Nitrogen formed during Combustion in Air.** By L. ILOSVAY DE NAGY ILOSVÁ (*Bull. Soc. Chim.*, 1894, [3], 11, 272—280).—See this vol., ii, 61.

**Schuller's Yellow Modification of Arsenic.** By H. MCLEOD (*Chem. News*, 1894, 70, 139).—The author obtained the yellow modification of arsenic, first discovered by Schuller, by heating arsenic in carbonic anhydride or in a vacuum. It reverts spontaneously to ordinary arsenic, the change commencing at the warmer part of the deposit, and extending gradually but rapidly to the cooler portion.

D. A. L.

**Hydrate of Carbonic Anhydride: Composition of Gaseous Hydrates.** By P. VILLARD (*Compt. rend.*, 1894, 119, 368—371).—The hydrate of carbonic anhydride discovered by Wroblewski (*Abstr.*, 1882, 1026) is analogous in its mode of formation and decomposition to the hydrate of nitrous oxide (*Abstr.*, 1894, ii, 278). Combination between the gas and water takes place under simple pressure, and neither hydrate decomposes below  $0^\circ$  under ordinary pressure, except in presence of liquid water. Both hydrates have the same crystalline form, and neither of them acts on polarised light.

Analyses of the hydrate of carbonic anhydride by the method used for the hydrate of nitrous oxide gave results varying between  $CO_2, 6\cdot2H_2O$  and  $CO_2, 5\cdot9H_2O$ , and the author concludes that the exact composition is  $CO_2, 6H_2O$ , and hence the compound is strictly analogous to the nitrous oxide hydrate. The heats of formation of the two compounds are the same,  $+15\cdot0$  Cal., from gas and from liquid water. The heat of dissolution under pressure is, in both cases, practically identical with the heat of fusion of the combined water.

A crystalline hydrate of sulphurous anhydride formed at  $0^\circ$  gave results varying between  $SO_2, 6\cdot1H_2O$  and  $SO_2, 6\cdot0H_2O$ , and a hydrate of methylic chloride gave results between  $MeCl, 6\cdot3H_2O$  and  $MeCl, 5\cdot9H_2O$ . It would seem, therefore, that the two hydrates have, respectively, the formulæ  $SO_2, 6H_2O$  and  $MeCl, 6H_2O$ . In both cases the crystals are without action on polarised light, and seem to have the same form as the hydrates of nitrous oxide and carbonic anhydride.

These results render it very probable that the hydrates of all gases,

except the hydracids, have the same constitution and are represented by the general formula  $M_6H_2O$ . C. H. B.

**Triammonium Orthophosphate.** By P. SCHOTTLÄNDER (*Zeit. anorg. Chem.*, 1894, 7, 343—344).—See this vol., ii, 64.

**Colloidal Silver.** By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 1894, 7, 339—340).—The organosol Ag (EtOH) (Abstr., 1892, 775), when treated with organic solvents, either remains in solution or coagulation takes place, and the production or absence of coagulation shows the existence or otherwise of an organosol with the organic solvent employed. No coagulation is observed with propylic, isobutylic, tertiary butylic, or cetylic alcohol, ethylene glycol, glycerol, or phenol. Coagulation takes place after a few hours with trimethylamide and pyridine. Coagulation takes place at once with isopropylic, normal and secondary butylic alcohols, trimethylcarbinol, heptylic, cetylic or allylic alcohol, erythrol, octane, amylene, formaldehyde, cœnanthaldehyde, acetone, ether, acetic acid, benzene, benzylic alcohol, meta-cresol, triethylamine, dimethylamine, diethylamine, and quinoline.

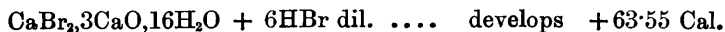
The solutions in which coagulation did not take place were observed for some months. With phenol, coagulation commenced after 14 days and gradually increased; and after one month coagulation was observed in the case of propylic and tertiary butylic alcohols. After two months, coagulation had taken place in all the solutions.

The organosol Ag (EtOH) was coagulated by ether, the precipitate washed with absolute ether and dried over sulphuric acid in a vacuum. It has a greenish, metallic lustre, loses 4·5 per cent. in weight when heated, and when allowed to remain in a damp atmosphere increases in weight to the extent of 15·82 per cent. The dry colloid is entirely soluble in water. E. C. R.

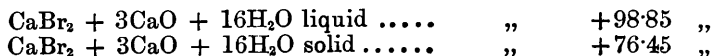
**Basic Calcium Salts.** By TASSILLY (*Compt. rend.*, 1894, 119, 371—373).—When three parts of calcium oxide is added in successive small portions to a solution of 100 parts of calcium bromide in 75 parts of hot water, the filtered liquid, on cooling, deposits acicular crystals of the oxybromide  $CaBr_2 \cdot 3CaO + 16H_2O$ , which may be washed with a 25 per cent. aqueous solution of calcium bromide.

The oxyiodide previously described (Abstr., 1894, ii, 92) may be more advantageously prepared in the same way as the oxybromide.

The oxybromide and oxyiodide are decomposed by water, alcohol, carbonic anhydride, and the stronger acids. The hydracids and very dilute nitric acid dissolve them readily, and sulphuric acid converts them into sulphates.



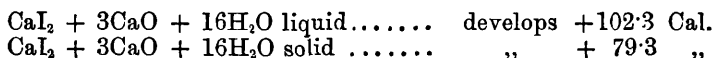
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Further



hence



It is noteworthy that the heat of dissolution of the oxy-salt in the corresponding hydracid is practically identical in the three cases, but the heat of formation from the proximate constituents increases with the atomic weight of the halogen. C. H. B.

**Action of Phosphorus Trichloride on Magnesium Nitride.** By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 1894, 7, 358).—When phosphorus trichloride is passed over magnesium nitride by the aid of a current of nitrogen, a violent action takes place at a red heat, and large quantities of phosphorus distil over. The residue consists of magnesium chloride and a bright, brown powder, which contains 19·26 per cent. of magnesium together with phosphorus and nitrogen. E. C. R.

**Stability of Aqueous Solutions of Mercuric Chloride.** By E. BURCKER (*Compt. rend.*, 1894, 119, 340—342).—Aqueous solutions containing 1 part of mercuric chloride and 1·14 parts of hydrogen chloride per litre of ordinary water (containing calcium carbonate) undergo only trifling alteration when exposed to air and light, and no alteration at all when kept in well-closed vessels in the dark. 0·5 gram of tartaric acid per litre has the same effect (compare Abstr., 1894, ii, 93 and 381).

Indigo-carmin has no decomposing effect on solutions of mercuric chloride in distilled water acidified with tartaric acid, even when they are exposed to light. C. H. B.

**The Molecular State of Mercurous Chloride Vapour.** By V. MEYER (*Ber.*, 1894, 27, 3143—3145; compare Harris and Meyer, Abstr., 1894, ii, 353).—The author adheres to the conclusion already drawn (*loc. cit.*), and referring to the experiments of Fileti (Abstr., 1894, ii, 449), points out that no amalgamation occurs when a cooled gold surface is immersed in the mixed vapours of mercury and mercuric chloride; the evidence of the stability of mercurous chloride adduced by Fileti is, therefore, no longer valid. M. O. F.

**Double Salts of Higher Chlorides of Manganese and Copper.** By G. NEUMANN (*Monatsh.*, 1894, 15, 489—494).—The compound  $(\text{NH}_4)_2\text{MnCl}_5$  is obtained when manganese dioxide is allowed to remain for a considerable time in contact with concentrated hydrochloric acid, kept cool by immersion in a freezing mixture of ice and salt, and saturated with hydrogen chloride and chlorine; the brown solution thus obtained, when filtered and treated with a cold solution of ammonium chloride, yields the compound in violet-brown crystals. It is readily decomposed, the violet-brown aqueous solution, even when kept cool, becoming turbid from separation of manganese dioxide. In a precisely similar manner, the double potassium manganese chloride,  $\text{K}_2\text{MnCl}_5$ , is obtained. The formation of these compounds confirms the results obtained by Pickering (*Trans.*, 1878, 654), and

disproves Fisher's statement that a tetrachloride of manganese is formed (Trans., 1878, 409).

On passing a mixture of hydrogen chloride and chlorine into a well-cooled solution of cupric chloride, glistening, red needles, which quickly change to green, are obtained. These have the formula  $\text{CuH}_2\text{Cl}_6$ , whereas on passing hydrogen chloride into a well-cooled solution of cupric chloride, Engel (Abstr., 1888, 558) obtained a salt to which he ascribed the formula  $\text{CuHCl}_3$ , and Sabatier (Abstr., 1888, 1036, 1037) stated that the product formed was  $\text{CuH}_2\text{Cl}_4$ . Cuprous chloride, free from cupric salt, gives with hydrogen chloride the compound  $\text{CuHCl}_2$ , which crystallises in pearly-grey needles. The two compounds  $\text{MnK}_2\text{Cl}_4$  and  $\text{CuH}_3\text{Cl}_5$  are of interest on account of their illustrating the heptad nature of manganese and the octad nature of copper respectively.

G. T. M.

**Constitution of Cobalt, Chromium, and Rhodium Bases.** By S. M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1894, 7, 289—330; Abstr., 1894, ii, 50).—Aquotetraminexanthocobalt salts are obtained from chloronitrotetraminecobalt chloride (Abstr., 1894, ii, 50), which is easily prepared by heating croceocobalt sulphate with concentrated hydrochloric acid.

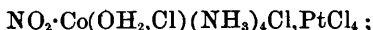
*Aquotetraminexanthocobalt chloride*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2\text{Cl})(\text{NH}_3)_4\text{Cl}$ , is obtained by warming the above chloride with water and a few drops of acetic acid, and allowing the solution to crystallise over sulphuric acid. If treated with concentrated hydrochloric acid, it is reconverted into the anhydrous chloride, and after drying in the air gives up its water when allowed to remain over sulphuric acid.

*Aquotetraminexanthocobalt hydrate*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2\text{OH})(\text{NH}_3)_4\text{Cl}$ , is obtained when the anhydrous chloride is treated with dilute ammonia in the cold. It crystallises in deep red prisms, is converted into the anhydrous chloride by concentrated hydrochloric acid, and gives with silver nitrate a mixture of silver chloride and silver oxide. The formation of this basic salt shows that the two chlorine atoms in aquotetraminexanthocobalt chloride, although they behave in the same way towards silver nitrate, are combined in a totally different manner, namely, the one to the ammonia chain, the other to the radicle  $\text{OH}_2$ . When the anhydrous chloride is shaken with freshly-prepared silver oxide, it yields a yellowish-brown filtrate, which is strongly alkaline, liberates ammonia from ammonium salts, and no doubt contains aquotetraminexanthocobalt hydrate.

The preparation and properties of the following salts are described. The *bromide*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2\text{Br})(\text{NH}_3)_4\text{Br}$ ; the *nitrate*,

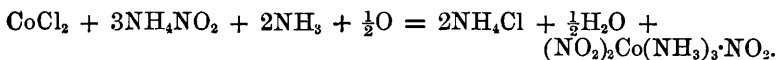


the *sulphate*,  $\text{NO}_2\cdot\text{Co}\left<\begin{smallmatrix} (\text{OH}_2) \\ (\text{NH}_3)_4 \end{smallmatrix}\right>\text{SO}_4$ ; the *platinochloride*,



the *aurochloride*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2\text{Cl})(\text{NH}_3)_4\text{Cl}\cdot\text{AuCl}_3$ ; the *diaminecobaltinitrite*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2)(\text{NH}_3)_4[(\text{NO}_2)_2(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2]_2$ ; and the *oxalate*,  $\text{NO}_2\cdot\text{Co}(\text{OH}_2)(\text{NH}_3)_4\cdot\text{C}_2\text{O}_4$ .

*Preparation of dinitrotriaminecobalt salts.*—Dinitrotriaminecobalt nitrite is obtained by the oxidation of an ammoniacal mixture of cobalt chloride, sodium nitrite, and ammonium chloride, employed in the proportions represented by the following equation,



The reaction varies, however, very considerably, according to the proportions of ammonium salt and ammonia employed, and under these varying conditions ammonium cobalt nitrite, ammonium diaminecobalt nitrite, croceocobalt chloride, xanthocobalt chloride, or croceodiaminecobalt nitrite is obtained. The triamine nitrite is also obtained by heating the ammonium diamine nitrite with water and concentrated ammonia on the water bath, also by boiling an aqueous solution of ammonium diamine nitrite and the flavonitrate with a few drops of acetic acid.

*Dinitrotriaminecobalt chloride*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_3\text{Cl}$ , is obtained by heating the triamine nitrite with hydrochloric acid. It crystallises in red tablets, yields all its chlorine as silver chloride when treated with silver nitrate, is converted into the triamine nitrite by sodium nitrite, and into the dichrochloride when warmed with concentrated hydrochloric acid. When warmed with ammonium nitrate and ammonia, and then treated with dilute nitric acid, it yields flavocobalt nitrate, whence the author concludes that the constitution of this salt is represented by the formula  $(\text{NO}_2)_2\text{Co}\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{Cl}$ .

The *dinitrotriamine bromide*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_3\text{Br}$ , and *dinitrotriamine sulphate*,  $[(\text{NO}_2)_2\text{Co}\cdot(\text{NH}_3)_3]_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ , are also described.

The last part of the paper deals with the views put forward by A. Werner (*Zeit. physikal. Chem.*, 1894, **14**, 506), and the structure of the ammonio-cobalt salts.

E. C. R.

**Molybdamide.** By H. FLECK and E. F. SMITH (*Zeit. anorg. Chem.*, 1894, **7**, 351—357).—When freshly-prepared molybdic chloride,  $\text{MoO}_2\text{Cl}_2$ , is treated with sodium ethoxide in ethereal solution, a precipitate of sodium chloride is obtained; the filtrate, on evaporation, yields a blue, amorphous compound, which is converted into ammonium molybdate when dissolved in alcohol and treated with ammonia.

*Molybdamide*,  $\text{OH}\cdot\text{MoO}_2\cdot\text{NH}_2$ , is obtained when molybdic chloride dissolved in chloroform is treated with dry gaseous ammonia or shaken with aqueous ammonia. A black precipitate is obtained which is probably the diamide; it is, however, very unstable, and when extracted with alcohol is converted into the monamide; the latter is a brownish-red, amorphous powder.

Molybdic chloride forms more stable compounds with ethylamine than with ammonia, a mono- or di-ethylamide being formed according to the amount of ethylamine employed.

The *monethylamide*,  $\text{OH}\cdot\text{MoO}_2\cdot\text{NHEt} + \frac{1}{2}\text{H}_2\text{O}$ , is a white powder, which gradually turns reddish-brown on exposure to air; it is soluble in water, and yields ethylamine when treated with alkalis.

The *diethylamide*,  $\text{MoO}_2(\text{NHEt})_2$ , is a reddish-brown powder, which gives off ethylamine on exposure to air, and gradually becomes white;

it reacts violently with nitric acid, yields ethylamine when treated with alkalis, and gives a deep blue solution with concentrated sulphuric acid.

E. C. R.

**Thorium Metaoxide and its Hydrate.** By J. LOCKE (*Zeit. anorg. Chem.*, 1894, **7**, 345—350).—Thorium metaoxide, which is obtained by heating the oxalate, is found to have the composition  $\text{Th}_3\text{O}_5$ . It is also obtained when the normal thorium oxide containing iron is heated in a current of steam, or when the pure normal oxide is heated in hydrogen. A quantitative determination of the water formed by the last method of reduction gave numbers agreeing with those required for the reduction of  $\text{ThO}_2$  to  $\text{Th}_3\text{O}_5$ .

Thorium metahydroxide is prepared by evaporating the metaoxide to dryness with hydrochloric acid, dissolving the residue in hot water and precipitating with ammonia. It is a pure white precipitate, and has the composition  $\text{Th}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ ; when dried at  $100^\circ$  it loses  $1\text{H}_2\text{O}$ . The metahydroxide,  $\text{Th}_3\text{O}_5 \cdot \text{H}_2\text{O}$ , is also obtained when the metaoxide is treated with hydrochloric acid, but if prepared by this method it forms a brownish residue resembling varnish.

E. C. R.

**Vanadium in Commercial Caustic Soda.** By H. L. ROBINSON (*Chem. News*, 1894, **70**, 199).—A solution of caustic soda became deep purple in colour when saturated with washed hydrogen sulphide, but on exposure to light with access of air the colour slowly faded, the liquid becoming yellowish, and a brown precipitate being formed; this was found to be due to the presence of vanadium, but this element apparently is not present as a vanadate.

D. A. L.

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## Mineralogical Chemistry.

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**Dimorphous Minerals.** By C. DOELTER (*Jahrb. f. Min.*, 1894, ii, Mem., 265—277).—The phenomenon of polymorphism, notwithstanding numerous theories, is not yet definitely elucidated. O. Lehmann, Mallard, and others have recently assumed that if two substances exhibit different crystalline forms they must also be chemically different. With diamond and graphite, P. Groth also classes andalusite and disthene among the chemically dimorphous substances. With a view to thoroughly investigate the matter, the author has submitted a number of dimorphous modifications, under conditions as nearly as possible similar, to the action of various agents, such as chlorine, hydrogen chloride, hydrogen fluoride, &c. The following minerals were treated. (1) Andalusite and cyanite, (2) orthoclase and microcline, (3) epidote and zoisite, (4) enstatite and anthophyllite, (5) diopside and actinolite, (6) iron pyrites and marcasite, (7) zinc-blende and wurtzite.

With marcasite and iron pyrites, the solubility in water and in sodium sulphide is identical, but the action of soda is quantitatively different. With zinc-blende and wurtzite, the differences are slight.

From the fact that on treatment with water and sodium sulphide new substances are formed which are identical with the modification employed in the experiment, the conclusion is arrived at that chemical difference of the dimorphous modifications of  $\text{ZnS}$  and of  $\text{FeS}_2$  also exist in the solutions of the two, as the conditions of temperature were the same in the experiments. Marcasite is notably less decomposed by soda solution than pyrites is. Cyanite and andalusite exhibit but slight differences in behaviour when treated with decomposing agents. With enstatite and bronzite, chemical differences probably exist. In the case of actinolite and diopside, no safe conclusion can be drawn on account of the varying proportions of magnesium and calcium.

B. H. B.

**Natural Oxides of Manganese.** By A. GORGEU (*Jahrb. f. Min.*, 1894, ii, Ref., 404—406; from *Bull. Soc. fran. min.*, 1893, 16, 96—104, 133—148).—The author has published a further instalment of the description of his investigation on manganese oxides (compare Abstr., 1890, 570; 1891, 270; 1894, ii, 19 and 99). Analyses are given of pyrolusite from various localities, of manganite from Ilfeld, of hausmannite from Ilmenau, and of braunite from S. Marcel and from Schwarzenburg.

B. H. B.

**Chromite in Lower Silesia.** By H. TRAUBE (*Jahrb. f. Min.*, 1894, ii, Ref., 411—414; from *Zeit. deutsch. geol. Ges.*, 1894, 50—67).—Chromite occurs in small quantities widely distributed throughout the serpentine of the Zobten Mountains. Recently a workable deposit has been found at the Schwarzenburg, near Tampadel. The chromite has a sp. gr. of 4.21, and contains

$\text{Cr}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{MgO}$ .	Total.
41.23	24.58	2.28	16.99	0.58	14.77	100.43

It resembles the chromite of Grochau. The associated minerals are fully described.

B. H. B.

**Formation of Magnesite and Dolomite.** By F. W. PFAFF (*Jahrb. f. Min.*, 1894, *Beilage*, 9, 485—507).—The author describes the experiments which he has had in progress for the past three years to obtain dolomite and magnesite artificially. The experiments did not differ essentially from those of v. Marlet (1847), Hoppe-Seyler (1875), Scheerer (1866), and others.

B. H. B.

**Davyn.** By H. TRAUBE (*Jahrb. f. Min.*, 1894, *Beilage*, 9, 475—479).—The author gives the results of an investigation of the figures produced on etching davyn. The material employed was obtained from Vesuvius, and hydrochloric, hydrofluoric, and nitric acids were used, the latter being found the most suitable. Analysis of carefully-selected material gave the following results.

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{Cl}$ .	$\text{SO}_3$ .	$\text{CO}_2$ .
33.12	28.60	9.91	11.91	7.22	5.14	2.38	2.88

B. H. B.



**Chemical Nature of Staurolite.** By C. RAMMELSBERG (*Jahrb. f. Min.*, 1894, *Beilage*, 9, 480—484).—In the staurolite of Lisbon, Penfield found dark carbon-bearing inclusions. In that of Mount Campione, the author found enclosed crystals of blue cyanite. From his analyses, Penfield deduced the formula  $H_2R''_2R_5Si_4O_{26}$ . The author now brings forward arguments to show why he is unwilling to accept Penfield's formula.  
B. H. B.

**Rocks and Minerals from the Karakoram Himalayas.** By T. G. BONNEY and Miss C. A. RAISIN (*Proc. Roy. Soc.*, 1894, 55, 468—487).—The authors describe a series of specimens of rocks and minerals collected by W. M. Conway during his journey in the Karakoram Himalayas. The rocks of special interest described are some consisting almost wholly of hornblende, specimens of piedmontite schist, and of schist with conspicuous secondary mica. Among the minerals, is an interesting pseudo-jade, a fragment found on a moraine; microscopic examination and chemical analysis show that this specimen cannot be referred to nephrite. It appears to be composed of a lime-garnet, a potash-jadeite, a mineral of the scapolite group, and a little pyroxene.  
B. H. B.

**Water and Sea-bottom Deposits from the Eastern Mediterranean.** By K. NATTERER (*Monatsh.*, 1894, 15, 530—595; compare *Abstr.*, 1893, ii, 216, and 1894, ii, 102).—In this communication, the author gives further particulars of analyses of water and sea-bottom deposits obtained during the voyage of the ship "Pola," in the Eastern Mediterranean during 1893.  
G. T. M.

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## Physiological Chemistry.

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**Simple Form of Gas Pump.** By L. HILL (*J. Physiol.*, 1894, **17**, 353—355).—This is a modification of the mercurial pump suitable for the examination of small quantities of blood. Its construction is figured.  
W. D. H.

**Heat Value of Nutritive Substances.** By F. STOHMANN (*Zeit. Biol.*, 1894, **31**, 364—391).—In addition to certain generalisations contrasting animal and plant life and their mode of nutrition, and the products they give rise to, the chief part of the present paper contains tables of the elementary composition and heat value of the most important animal and vegetable proteïds, albuminoids, derivatives of these such as urea, and the amido-acids, animal and vegetable fats and carbohydrates. Berthelot's apparatus was used.  
W. D. H.

**Heat Production in the Chick before and after Hatching.** By M. S. PEMBREY, M. H. GORDON, and R. WARREN (*J. Physiol.*, 1894, **17**, 331—348).—Up to the 20th or 21st day of incubation, the  
5—2

chick responds to changes of external temperature like a cold-blooded animal; then there is an intermediate stage when no response is obtained, and when the chick is hatched it responds like a warm-blooded animal. The method used was a modification of Haldane's apparatus. W. D. H.

**Blood Coagulation.** By L. LILIENFELD (*Zeit. physiol. Chem.*, 1894, 20, 89—165; compare Abstr., 1894, ii, 22).—In this paper, in addition to a historical account of the question, a full description of experiments and theories is given, part of which has appeared in several preliminary communications. The active agent in coagulation is regarded as a nucleo-albuminous substance, named *nucleo-histon*; it is considered to originate from leucocytes, especially from their nuclei, and from platelets. The nuclein in this substance hastens, whilst the histon hinders, coagulation; the separation into nuclein and histon can be effected by lime water or baryta water. Nuclein alone, and calcium chloride alone, do not cause coagulation in solutions of Hammarsten's fibrinogen; but if acetic acid is added to a solution of fibrinogen, a substance is precipitated which is coagulated by nuclein with calcium salts, or by calcium salts alone. This substance is termed thrombosin; and fibrin is regarded as a calcium compound of thrombosin. The constituent of fibrinogen which remains in solution when thrombosin is precipitated by acetic acid, is like peptone in some of its properties, particularly in its hindering influence on coagulation. Nuclein, or rather nucleic acid, acts just like acetic acid, precipitating free thrombosin from fibrinogen (not a nucleic acid compound of thrombosin). This holds both for intravascular and extra-vascular coagulation; nucleic acid first splits up the fibrinogen molecule, and then one of its components, thrombosin, unites with a calcium salt to form fibrin. The fibrin-ferment is described as a globulin which is a product and not the cause of coagulation. W. D. H.

**Glucose.** By F. RÖHMANN (*Ber.*, 1894, 27, 3251—3253).—The author, in conjunction with Bial, has recognised the presence of an enzyme in blood-serum and lymph, which has the power of transforming starch into glucose (Abstr., 1893, i, 187). He now states that the enzyme affects glycogen in a similar manner. Bial has already shown (Abstr., 1893, ii, 333, 581) that blood-serum transforms dextrin and maltose into glucose. The author finds that by the action of saliva on starch paste, isomaltose, maltose, and dextrin are formed, together with a small amount of glucose; whilst by the action of pancreatic juice and intestinal juice (*succus entericus*) on starch paste, a larger quantity of glucose is formed but not so large as that resulting from the action of blood-serum. Following, however, the velocity of the liquefaction of starch paste and of the increase in the cupric reducing power, it is found that pancreatic juice acts more powerfully than saliva, the latter, however, liquefies starch paste more rapidly than blood-serum. Furthermore, saliva and pancreatic juice bring about a quicker rise of the cupric reducing power of the transformation products to a maximum, but this is lower than the

maximum attained by the action of blood-serum over a considerably longer period.

According to the author, the simplest explanation of these results is that saliva, pancreatic juice, intestinal juice, and blood-serum contain both diastase (maltase) and glucase, the former being present in largest amount in the pancreas, and in the smallest in the blood, and *vice versâ* as regards glucase. By allowing fresh yeast cells to remain over alcohol, whereby the glucase is destroyed, the aqueous extract no longer acts on maltose but only on saccharose. Invertase and diastase can thus be prepared free from glucase.

A. R. L.

### **Action of Calcium and other Salts on the Animal Organism.**

By H. WEISKE (*Zeit. Biol.*, 1894, **31**, 421—448).—A number of rabbits were fed on oats, a diet which is acid and poor in calcium, and the observations showed that they lost weight; a comparison being made with other animals who received in addition calcium carbonate, calcium sulphate, strontium carbonate, or magnesium carbonate. At the end of the research the composition of their bodies, and especially of the skeleton, was examined. The salts administered correct the acidity and harmfulness of the oats; calcium carbonate having the best effect, both as regards the general condition of the animals and the amount of calcium in the skeleton. The bones show also that strontium and magnesium can replace part of the calcium. The urine and fæces also show evidence of the different salts administered.

W. D. H.

**Calcareous Concretions in the Brain.** By F. B. MALLORY (*J. Pathol. and Bacteriol.*, 1894, **3**, 110—117).—These not uncommon deposits are due to the calcareous infiltration of colloid material (hyaline of v. Recklinghausen) which is deposited in the blood vessels. In the larger vessels, the middle coat is earliest and most affected.

W. D. H.

**Salivary Glands of the Leech.** By J. M. CROCKEWIT (*Tijdschr. d. Ned. Dierk Vereen.*, 1894, 296—312).—It is the secretion of these glands which prevents the coagulation of the blood. Most of the present paper is anatomical. Some observations of a chemical nature seem to indicate that the substance to which the secretion owes the activity alluded to above is a nucleo-albumin.

W. D. H.

**Calcium in the Liver Cells of the Ox.** By F. KRÜGER and W. LENZ (*Zeit. Biol.*, 1894, **31**, 392—399).—The ox in different states of development furnished the material for the research. The calcium in the liver cells of the calf is about 70 per cent. greater than in the fully-grown animal. The foetal period shows two maxima, namely, in the fifth and tenth months; at these times, there is 45 per cent. more calcium than in the adult; the minima also appear to be two occurring in foetuses of 20—30 and 60—70 cm. long respectively. The amount of calcium varies inversely with that of the iron during the foetal period; they are described as antagonistic. Sex and pregnancy make no difference.

W. D. H.

**Percentage of Sulphur and Phosphorus in the Hepatic and Splenic Cells at different Ages.** By F. KRÜGER, F. SZYMKEWICZ, L. V. LINGEN, and H. WALTER (*Zeit. Biol.*, 1894, **31**, 400—412).—The amount of sulphur in the liver cells of oxen remains fairly constant throughout life, and in different individuals of the same age varies within certain narrow limits. Phosphorus is more variable; the foetal cells are richest, and during foetal life the percentage is fairly constant; it is less in the calf, less still in the grown ox. Sex makes no difference.

With regard to the spleen, again sulphur varies but little, being, however, rather less abundant in calves than in the foetal and full-grown periods. Phosphorus is most abundant in foetuses between 30 and 60 cm. long, sinks at birth, rises suddenly after birth, and is lowest of all in the grown animal. Sex has no influence.

During the foetal period, the sulphur in the splenic cells is about 16 per cent. higher than in the liver cells; after birth, the two are about equal, and in grown cattle the splenic cells are about 9 per cent. richer in sulphur than the liver cells. Foetuses of 30—60 cm. length have 39 per cent. more phosphorus in the splenic than in the liver cells. In foetuses of 80—90 cm. length, the amount of phosphorus is about the same in the two varieties of cells; whilst in foetuses of 90—100 cm. length, the liver cells contain 16 per cent. more phosphorus than the splenic cells. After birth, the splenic cells again contain more phosphorus by 25 per cent. than the liver cells; in grown cattle, there is an approximate equality, although the total amount of phosphorus is less than in calves and foetuses.

In adult men, the liver cells contain 2·41 of sulphur, 1·28 of phosphorus, and 0·077 of iron per cent. In the liver of new-born children, the numbers are respectively 3·56, 1·54, and 0·314. The adult man and ox are in this connection very much alike. In fatty degeneration of the liver, the numbers were 2·18, 0·87, and 0·176, that is, sulphur and phosphorus fall, whilst iron rises.

W. D. H.

**Casein of Human Milk.** By A. WROBLEWSKI (*Inaug. Diss.*, Bern, 1894).—The mean of analyses of the casein of human milk gives C, 45·01; H, 7·31; N, 15·07; P, 0·8; S, 4·7; O, 27·11 per cent. It differs from the casein of cow's milk in solubility, and in the fact that on peptic digestion it yields no residue of nuclein.

W. D. H.

**Phosphorus in Digestion Products of Casein.** By W. v. MORACZEWSKI (*Zeit. physiol. Chem.*, 1894, **20**, 28—51).—A series of five experiments show that the amount of phosphorus in the nuclein left after the digestion of casein by artificial gastric juice is variable, and that all the phosphorus of the casein is not in the form of nuclein; from 6 to 60 per cent. of the phosphorus is present in this form. The casein of human milk contains phosphorus but no nuclein (compare Wroblewski, preceding abstract).

W. D. H.

**Egg-shells of Echidna and other Vertebrates.** By R. NEUMEISTER (*Zeit. Biol.*, 1894, **31**, 413—420).—The egg-shells of *Echidna aculeata* (*E. hystrix*) consist of a keratin-like substance containing

5 per cent. of sulphur. It is, however, digested neither by gastric nor by pancreatic juice; some other keratins are similarly resistant. In invertebrates, the organic basis of egg-shells is chitin or some other skeleton. Keratin appears to be only present in the egg-shells and membranes of vertebrate animals. In the frog only has mucin been described. The eggs of some birds and reptiles are briefly referred to in this connection. Calcium carbonate is the principal inorganic constituent.

W. D. H.

**Acidity of Urine.** By V. LIEBLEIN (*Zeit. physiol. Chem.*, 1894, 20, 52—88).—This gives a long and critical account of the various methods, chemical and colorimetric, by means of which the acidity of urine, and the various factors of which it is made up, can be determined. The following general conclusion is drawn, that by the estimation of phosphoric acid in the form of diphosphate alone, can a trustworthy measure of the acidity of urine be obtained.

W. D. H.

**Ethereal Hydrogen Sulphates in Urine.** By J. EIGER (*Chem. Centr.*, 1894, i, 873; from *Pharm. Zeit. f. Russland*, 23, 149—151).—The ethereal hydrogen sulphates in the urine are increased in most diseases of the liver; the liver, under normal circumstances, probably oxidises aromatic substances. In intestinal catarrh and in kidney diseases (especially chronic ones), these constituents of the urine are also increased. By disinfection of the alimentary canal and rapid removal of its contents, the ethereal hydrogen sulphates are diminished.  $\alpha$ - and  $\beta$ -naphthol, hydrochloric acid, hydrogen phosphate, and sulphuric acid cause an increase; quinine nitrate and lactic acid, a decrease in these sulphates. Calomel produces the latter result when it causes purgation also. Potassium iodide, arsenic, ipecacuanha, digitalis, (wallaria, *Adonis vernalis*, opium, morphine, codeine, and bismuth salicylate have no effect.

W. D. H.

**Hæmatoporphyrin in Normal Urine.** By A. E. GARROD (*J. Physiol.*, 1894, 17, 349—352).—Renewed research confirms the author's previous conclusion that hæmatoporphyrin is a scanty but normal constituent of urine. 20 c.c. of a 10 per cent. solution of sodium hydroxide are added to every 100 c.c. of urine; the precipitated phosphates are collected and washed with water. The precipitate is dissolved in rectified spirit and acidified with hydrochloric acid; the solution shows the bands of acid hæmatoporphyrin. Ammonia is then added to precipitate the phosphates, and acetic acid to redissolve them; chloroform then extracts hæmatoporphyrin completely, and shows the bands of the alkaline pigment.

W. D. H.

**Pigmentation of Uric acid Crystals Deposited from Urine.** By A. E. GARROD (*J. Pathol. and Bacteriol.*, 1894, 3, 100—106).—Of the true urinary pigments which exist ready formed in urine, only the normal yellow pigment (urochrome) and uroerythrin appear to possess the property of colouring uric acid crystals deposited from their solutions. The yellow pigment being a constant constituent of

urine always furnishes the ground tint of the crystals, and plays the more important part in determining their form, the whetstone or canoe shape being specially the one produced. In the majority of instances, uric acid crystals which are spontaneously and rapidly deposited from urine, contain uroerythrin also, to which they owe their red colour when seen in bulk. It is, however, never the sole colouring matter in these sediments, and varieties of tint are due to differences in admixture of it with urochrome. The minute quantity of iron present in the crystals is a constituent of neither pigment. Urobilin and hæmatoporphyrin take no part in the coloration of the crystals, but other pigments occasionally present in urine may share in the coloration, such as the brown products caused by the action of mineral acids, the oxidation products of phenol-derivatives, and the pigments of the bile.

W. D. H.

**Percentage of Iron in the Liver in Aukyllostomiasis.** By B. RAKE (*J. Pathol. and Bacteriol.*, 1894, **3**, 107—109).—The percentage of iron in liver and spleen in five cases of disease, due to the presence of the worm *Aukyllostoma duodenale*, is given. The interest of such an investigation arises from the fact that the symptoms produced are very like those of pernicious anæmia.

	1.	2.	3.	4.	5.	Average percentage.
Liver....	trace	0.26	0.2068	0.0123	0.0228	0.100
Spleen...	0.04	3.28	—	0.0592	0.071	0.862

The average percentage of iron in the liver is less than in other diseases, and much less than in pernicious anæmia; thus: aukyllostomiasis, 0.1; other diseases, 0.12; pernicious anæmia, 0.7. The iron in the spleen is scarcely affected.

The intense anæmia associated with the disease is simply due to loss of blood from the intestine, and is not caused by any toxic substance causing blood destruction in the liver.

W. D. H.

**Piperazine as a Solvent of Uric acid Stones in Urine.** By J. FAWCETT (*Brit. Med. J.*, 1894, ii, 1426).—An aqueous solution of piperazine dissolves uric acid stones, but a solution of this substance in urine of the strength of 1 in 1000, which is above that usually found in the urine after taking the drug internally, has no effect whatever.

W. D. H.

**Physiological Action of certain Pyridine, Naphthalene, and Quinoline Derivatives.** By R. COHN (*Ber.*, 1894, **27**, 2904—2919; *Zeit. physiol. Chem.*, 1894, **20**, 210—218; compare Abstr., 1893, ii, 544).—In rabbits, quinaldine is entirely destroyed in the organism. In dogs, this is probably the case also, but the examination of the urine was more difficult, and the result somewhat uncertain. 1-Methylquinoline is in dogs entirely destroyed in the body. 3-Methylquinoline is changed into the corresponding quinoline-3-carboxylic acid in small measure (7 per cent.); the rest is destroyed.

W. D. H.

**Action of Drugs on the Heart of Daphnia.** By J. W. PICKERING (*J. Physiol.*, 1894, **17**, 356—359).—The heart of *Daphnia* can be easily observed with the microscope in the intact animal. The heart of each animal has an individual rhythm which, if external circumstances are unvaried, remains constant. Atropine sulphate, in doses of 0·3 milligram, increases the cardiac frequency; but after a period of from 20 to 30 minutes the heart becomes irregular, and, finally, stops in diastole and its irritability is lost. Muscarine nitrate, in large doses, has practically no effect on the heart, although it causes violent intestinal action, and, finally, loss of general irritability. Veratrine, in doses of 2 milligrams, does not seriously impair the cardiac rhythm; its depressing action is removable by heat. Caffeine causes, in small doses, increase of force and frequency; in large doses, tonic contraction and systolic stoppage; theobromine and xanthine have no effect. W. D. H.

**Pharmacological Investigation of Manaca Roots.** By J. BRANDL (*Zeit. Biol.*, 1894, **31**, 251—292).—The substances separated were manacin,  $C_{22}H_{33}N_2O_{10}$ , manacein,  $C_{15}H_{25}N_2O_9$ , a fluorescent substance identical with the æsculetin of Zwenger (*Annalen*, **90**, 63), valeric acid, and a material resembling humous substance. Leonardson (*Inaug. Diss.*, Dorpat, 1894), who has worked at the same plant, gives the formula for manacin as  $C_{15}H_{23}N_4O_5$ . Manacin is convertible into manacein by the action of certain micro-organisms. In addition to botanical details, the bulk of the research refers to the physiological actions of manacin, the most marked of which is a stimulating action of the motor end plates and of secreting glands. Manacein causes very similar results. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Bactericidal Action of Light and Air.** By R. F. D'ARCY and W. B. HARDY (*J. Physiol.*, 1894, **17**, 390—393).—Marshall Ward has shown that the bactericidal power of light is a peculiar property of light of short wave length, and is at its maximum at the violet end of the blue. This is only manifested in the presence of oxygen, and Würster (*Ber.*, 1886, **19**, 3201) has shown that “active oxygen” is produced when evaporation takes place in direct sunlight. The present experiments show that when the spectrum of a powerful arc light is allowed to fall on a moist surface in the presence of a delicate indicator, oxidation occurs, and the action commences at the blue end of the green, and continues through the blue, violet, and ultra-violet regions; in other words, the action is confined to a portion of the spectrum which corresponds with the region of activity in Ward's experiments.

W. D. H.

**Effect of Sunlight on Tetanus Cultures.** By F. F. WESBROOK (*J. Pathol. and Bacteriol.*, 1894, **3**, 70—77).—The experiments confirm other observers in the conclusion that oxygen is a necessary factor in the destruction of bacteria by light. Without oxygen sunlight is powerless. Moreover, the oxygen in the contained air shows diminution during the exposure of cultures. W. D. H.

**Thermophilic Bacteria.** By A. MACFADYEN and F. R. BLAXALL (*J. Pathol. and Bacteriol.*, 1894, **3**, 87—99).—The paper gives an account of bacteria which flourish at a high temperature in manures, in the causation of spontaneous combustion, &c. It is difficult to believe that they are merely freaks which only develop when a bacteriologist appears on the scene with an incubator. Their wide distribution, their good growth at these high temperatures, and their active fermentative properties, all point to their fulfilling some useful function in the economy of nature. W. D. H.

**Antiseptic Action of Phenyl-substituted Fatty Acids.** By J. P. LAWS (*J. Physiol.*, 1894, **17**, 360—363).—Phenylbutyric acid restrains the growth of anthrax bacilli when present in the proportion of 1 to 2500; it kills the sporeless bacilli in 30 minutes in a solution of 1 to 1000, and in 10 minutes in a solution of 1 to 700.

The following table compares its action with related substances.

	Phenol.	Phenylacetic acid.	Phenylpropionic acid.	Phenylbutyric acid.
Restraining power..	1—700	—	1—1900	1—2500
Killing power.....	1—200	1—450	1—600	1—1000
Length of exposure.	45 mins.	30 mins.	30 mins.	30 mins.

Antiseptic power thus increases with molecular weight; in the fatty acid series itself, the converse holds good (Duggan, *Amer. Chem. J.*, **7**, 62). W. D. H.

**Assimilation of Free Nitrogen by Algæ.** By A. KOCH and P. KOSSOWITSCH (*Bot. Zeit.*, 1893, **51**, 321—325).—The authors' experiments were as follows. Pure, ignited sand with nutritive salts (including calcium nitrate) was put into a number of Erlenmeyer flasks (60 grams of sand to each); in two experiments, sugar (0.05 gram) was added. The sand was seeded with algæ from a chalk heap, the flasks closed, and a slow current of purified air passed through. There was an arrangement for absorbing any ammonia which might be evolved. Three flasks were kept dark, and three near a window for nearly  $3\frac{1}{2}$  months. In the flasks kept dark (and consequently free from algæ), there was no gain of nitrogen, whilst there was a distinct gain in the other flasks in which algæ developed—the greater the development of algæ, the greater the fixation.

N. H. J. M.

**Fixation of Free Nitrogen by Algæ.** By P. Kossowitsch (*Bot. Zeit.*, 1894, 52, 97—116).—Frank (*Ber. d. bot. Ges.*, 1889, 34), and Schloesing and Laurent (*Abstr.*, 1892, 1021; 1893, ii, 363) have shown that soil bearing a growth of green or bluish-green algæ gained nitrogen from the free nitrogen of the air, and the results were confirmed by Koch and Kossowitsch (preceding abstract); but the question whether the soil bacteria took any part in the fixation remained undecided.

In the present paper, results are described which were obtained by using (1) pure cultivations of algæ, and (2) impure cultivations with soil bacteria. As in the previous experiments (*loc. cit.*), thin layers of pure sand were employed with nutritive matter, which had to be varied according to the requirements of the algæ. Thus, whilst *Stichococcus* prefers the phosphate,  $\text{KH}_2\text{PO}_4$ , *Cystococcus* prefers  $\text{K}_2\text{HPO}_4$ . The addition of sugar was favourable to some forms, but had no effect on others.

In the first series of experiments, which comprised 18 flasks seeded with *Cystococcus*, there was no fixation of nitrogen, either with or without sugar. The algæ grew well so long as they were supplied with nitrate, but no longer.

In the other experiments, the sand was seeded with mixtures of algæ and bacteria, obtained partly from the chalk heap (*loc. cit.*) and partly from arable soil, the experiments being conducted similarly to those with *Cystococcus*. There were five pairs of experiments, the one of each pair having sugar, the other none. In 1 and 2, a pure cultivation of *Cystococcus* and a soil extract were employed for seeding; 3 and 4 were seeded from the silica employed in isolating *Cystococcus*; 5 and 6 from a sand culture of *Stichococcus*, which had proved to contain soil bacteria; 7 and 8 were seeded from a thick, gelatinous skin which had formed on sand seeded a year before from the algæ of the chalk heap; 9 and 10 were seeded from a mixture of algæ and bacteria from arable soil, which resembled the mixture used for 8 and 9. The following are the results obtained.

No. of expts.		Nitrogen (milligrams).		
		At commence- ment.	At conclusion.	
			Without sugar.	With sugar.
1, 2	<i>Cystococcus</i> , Phormidium, soil bacteria and mould	2·6	7·1	9·5
3, 4	<i>Cystococcus</i> and bacteria .....	2·6	3·1	8·1
5, 6	<i>Stichococcus</i> and bacteria.....	2·6	2·3	2·7
7, 8	<i>Nostoc</i> , large round algæ, Scenedesmus and soil bacteria	2·6	?	19·1
9, 10	<i>Nostoc</i> and soil bacteria .....	2·6	8·8	25·4

The results of both series of experiments show that neither *Cysto-*

*coccus* nor *Stichococcus* have the power of fixing nitrogen. Both in the author's and in Schloesing and Laurent's experiments, the greatest amount of fixation was observed when *Nosioc* was present. It is possible that *Nostoc* and some other algæ have the power of fixing nitrogen, but as yet there is no evidence of fixation by algæ in absence of bacteria, and the author is inclined to the opinion that it is the bacteria which assimilates free nitrogen. The evidence in favour of this view is the beneficial effect of sugar in Experiments 3 and 4. In the first series, with pure cultivations of *Cystococcus*, there was no fixation either with or without sugar. In Experiments 3 and 4 of the second series (see table), there was without sugar scarcely any fixation, with sugar considerable fixation, indicating that not the *Cystococcus*, but the bacteria, fixed nitrogen. With mixed algæ and bacteria, there was considerable fixation, both with and without sugar. The conclusion drawn is that here some algæ, especially the gelatinous ones, take the place of sugar in supplying nutriment to the bacteria. This theory would account for the fact that similar soils exposed to and screened from light gain and do not gain respectively. In the first case algæ develop, in the second case no algæ are found, and without the carbonaceous food for the bacteria, fixation cannot take place. It was observed that the gelatinous substance of the algæ was full of bacteria. There is, therefore, a symbiotic relation between soil bacteria and certain algæ similar to that of the *Leguminosæ* and the nodule bacteria.

Berthelot (Abstr., 1893, ii, 429) and Gautier and Drouin (*ibid.*, 1888, 746 and 871) showed that the fixation of nitrogen in soils depends on the presence of organic matter.

N. H. J. M.

**Assimilability of Potassium in Poor Sandy Soils by the Action of Nitrates.** By P. PICHARD (*Compt. rend.*, 1894, 119, 471—473).—It was previously shown (Abstr., 1893, ii, 548) that newly-formed nitrates are the most readily assimilated. The results of experiments now described show that the potash of siliceous rocks is rendered available by nitrification, or by the application of nitrates. Tobacco was grown in the white sand of Bollène; in the first series the sand was manured with the nitrates of sodium, calcium, and magnesium, and with superphosphate; in the second, with organic nitrogen and the phosphates of sodium, calcium, and magnesium; whilst in the third series potassium was applied as nitrate, sulphate, and phosphate, nitrogen being present as nitrate, and in cake. The most striking results were obtained with the first series, in which no potash was applied. There was 5.6 grams of potassium present, insoluble in aqua regia; of this, 0.66, 3.21, and 0.48 gram was assimilated by the tobacco manured respectively with calcium, sodium, and magnesium nitrates. In the second series (nitrogen applied in organic form), there was active nitrification; of 5.6 grams of potash, insoluble in aqua regia, the plants took up from 1 to 3 grams, the greatest amount being assimilated under the influence of calcium carbonate. It is concluded that potassium is absorbed by plants in the form of nitrate. The sandy soils of Bretagne, with plenty of organic nitrogen,

give immensely increased yields of roots when treated with chalk and lime, especially when gypsum is added.

Taking into account the assimilability of potassium in the form of silicate under the influence of nitrates, the total potash of soils should be determined, as well as the potash dissolved by acids.

N. H. J. M.

**Effect of Chlorides on Vegetation and on the Amount of Starch in Potatoes.** By J. SCHULTE (*Bied. Centr.*, 1894, 23, 706—707; from *Magdeb. Zeit.*, 1894, No. 244).—Field experiments were made in which peas, rye, and barley were grown without manure, and with calcium, magnesium, and sodium chlorides, magnesium and calcium sulphate respectively (470 cwt. per acre). Potatoes were grown without and with the same minerals, farmyard manure being applied in each case as well. The results, showing yield of grain and of potatoes, percentage and yield of starch in potatoes per Morgen, are given in a table. The figures show that the employment of chlorine compounds in the potassium salts\* have no injurious effect at all, and that the magnesium chloride plot gave in most cases the highest yields, and, in the case of potatoes, much the greatest yield of starch.

N. H. J. M.

**Effect of the Degree of Ripeness and of Manures on the Physical and Chemical Properties of Barley Meal.** By C. KRAUS and A. STELLWAAG (*Bied. Centr.*, 1894, 23, 667—670; from *Zeits. landw. Ver. Bayern*, 1894, 164—171).—Lower Franconian barley was grown without manure, and with sodium nitrate (120 kilos. per hectare), and Chevalier barley without manure, and with guano (300 and 500 kilos.). The ears were examined at three or four periods of ripeness; the dry matter, flintiness, starch, proteids, and weight of grains per thousand being determined. The flintiness increased with the ripeness of the grain, and was not influenced in the case of Chevalier barley by the difference in manuring.

As regards chemical composition, this is improved by ripening, the quantity of starch increasing whilst the nitrogen diminished. The best composition is not obtained as a rule until the grain is yellow-ripe. Generally speaking, heavy manuring gives better yields if the crop is not laid; in this case, light grains rich in nitrogen are produced. With increased percentage of nitrogen, the grains are more flinty.

N. H. J. M.

**Nutritive Value of Cocoa.** By H. COHN (*Zeit. physiol. Chem.*, 1894, 20, 1—27).—The constituents of cocoa were separated by methods which are described, and their amount estimated. The beans and powdered cocoas of commerce were used; the former contained 48—50 per cent. of fat, and 10·8 of proteid; the latter, 32—33 per cent. of fat, 13·8 of proteid, and 12 of starch. Experiments in relation to its nutritive value were carried out in the usual way; the fat was found to be well digested, but the proteid not, nearly 50 per cent. of the latter being unused.

W. D. H.

**Secondary Products containing Nitrogen formed during Combustion in Air.** By L. LOSVAY DE NAGY LOSVA (*Bull. Soc.*

\* According to the text: there is no reference to potassium salts in the table.

*Chim.*, 1894, [3], **11**, 272—280).—The author has estimated the amount of ammonia and of nitrogen oxides formed during the combustion of some fuels. The following table gives the results, calculated in grams, of product per kilo. of fuel.

	Nitrogen as nitrogen oxides. Gram.	Nitrogen as ammonia. Gram.	Total combined nitrogen. Gram.
Charcoal dried at 120°.....	0·1190	0·6481	0·7671
Charcoal heated at 600° for 2 hours .....	0·1279	0·3679	0·4958
Charcoal heated at 900° for 2 hours .....	—	0·0229	0·0229
Coke heated at 600° for 2 hours	0·1756	0·1289	0·3045
Coal-gas.....	0·0771	0·0052	0·0823
Hydrogen .....	0·3286	0·0236	0·3522
Carbonic oxide.....	0·0147	—	0·0147

Volume for volume, hydrogen and coal-gas produced the same weight of ammonia, and almost the same weight of nitrogen oxides. Carbonic oxide, on the other hand, produces less than half as much nitrogen oxide, and, of course, no ammonia. The ammonia formed during the combustion of coke or charcoal is probably only a product of the decomposition of these substances. Coal yields a much larger proportion of ammonia, of which a large part is produced during the destructive distillation antecedent to the true combustion of the coal.

From these figures (basing his calculations on the amount of coal mined each year, which he takes as 390,000,000 tons), the author calculates the quantity of combined nitrogen (assimilable by plant life) formed annually by the combustion of fuel to be 290,000 tons. Lawes and Gilbert calculated the combined nitrogen taken up annually by the soil to be 1,000,000,000 tons, whilst Boussingault's figure makes it 164,000,000 tons. The author thinks that his own total is probably largely increased by the nitrogen oxides produced during storms, by the amount of ammonia produced from the burning of coal being larger than the figure 0·7671, which he used, and from other sources, but that the figure of 1,000,000,000 tons is largely in excess of that actually absorbed by the soil.

L. T. T.

### Analytical Chemistry.

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**Estimation of Chlorine in Urine.** By E. BÜDTKER (*Zeit. physiol. Chem.*, 1894, 20, 193—202).—Mohr's method gives too high results, as the urine contains substances which hinder the end reaction, probably by dissolving silver chromate. To incinerate the urine first is a tedious process, and results as good are obtained by the following method, the principle of which is to perform the reverse

of what is usually done, namely, to estimate silver by means of sodium chloride. The urine is first made strongly acid with nitric acid, and excess of silver solution added; in the presence of nitric acid, and absence of bromides, iodides, and thiocyanates, silver chloride is alone precipitated. By careful neutralisation of the filtrate with a feeble alkali, such as magnesia, a liquid is obtained in which the excess of silver can be estimated by titration with sodium chloride.

W. D. H.

#### **Sodium Thiosulphate for Standardising Iodine Solutions.**

By C. MEINEKE (*Chem. Zeit.*, 1894, **18**, 33—34).—Sodium thiosulphate may be completely freed from adhering moisture by treating the powdered substance, first with 96 per cent. alcohol, and then removing the excess of the latter by washing with ether. The ether is finally completely expelled by a current of dry air.

The product is absolutely free from mechanically adhering water, and, if satisfactory in other respects, constitutes a valuable reagent for ascertaining the strength of iodine solutions.

L. DE K.

**Estimation of Sulphur in Pyrites.** By F. JOHNSON (*Chem. News*, 1894, **70**, 212).—One gram of pyrites is treated in a flask with 25 c.c. of nitric acid; after a quarter of an hour, 1.5 grams of potassium chlorate is added, the whole warmed for a quarter of an hour, and then evaporated to dryness; 20 c.c. of hydrochloric acid is added and boiled off, and another 20 c.c. added and half boiled off, the residue is diluted with 50 c.c. of water, filtered, and washed. The solution is then made up to 200 c.c., heated with 1.5 grams of sodium hypophosphite, slight excess of barium chloride added, and after three hours the clear liquid is decanted on to a filter, whilst the precipitate is treated with 1 c.c. of hydrochloric acid and 100 c.c. of boiling water, being filtered after five minutes.

D. A. L.

**Indole as a Test for Nitrites.** By O. BUJWID (*Chem. Zeit.*, 1894, **18**, 364).—Indole gives a very delicate and beautiful reaction with traces of nitrites in water analyses. It is best to use a diluted alcoholic solution containing about 0.1—0.2 gram of indole per litre. Ten c.c. of the sample of water is mixed with a few drops of hydrochloric acid, and heated to 70—80°. A few drops of the reagent is now added, when, if nitrite is present, a beautiful red coloration is obtained, which in a few minutes will get somewhat darker. The author thinks that the reaction may also be utilised quantitatively.

L. DE K.

#### **Estimation of Carbonates and Caustic Alkalis in Mixtures.**

By P. L. ASLANOGLU (*Chem. News*, 1894, **70**, 166—167).—Titrating total alkalinity with N/10 sulphuric acid, with methyl-orange as indicator, and then the alkalinity due to hydroxide with phenolphthaleïn as indicator, gives erroneous results. Therefore, in place of the second titration, the author suggests estimating the carbonic anhydride in a Schrötter's apparatus, using methyl-orange to indicate the end of the action; he has obtained good results. Hydrochloric acid, or nitric



acid distilled from urea nitrate, and not sulphuric, should be used for expelling the carbonic anhydride. D. A. L.

**Estimation of Carbonates and Caustic Alkalis in Mixtures.** By C. A. SEYLER (*Chem. News*, 1894, 70, 187—188).—Phenolphthalein, although not to be highly recommended as an indicator for the estimation of carbonates in presence of hydroxides, is capable of giving accurate results if precautions are taken to prevent any loss of carbonic anhydride (compare preceding abstract). D. A. L.

**Triammonium Orthophosphate and the Detection of Magnesium.** By P. SCHOTTLÄNDER (*Zeit. anorg. Chem.*, 1894, 7, 343—344).—When examining a solution for magnesium with ammonium phosphate, a precipitate of triammonium orthophosphate is sometimes obtained having the appearance of magnesium ammonium phosphate, and may thus lead to errors; this precipitate is especially liable to occur in the presence of much ammonium chloride and strong ammonia.

Triammonium orthophosphate,  $(\text{NH}_4)_3\text{PO}_4 + 3\text{H}_2\text{O}$ , is obtained by adding ammonium chloride to an ammonium phosphate solution, warming the mixture at  $60^\circ$ , and then adding ammonia. It crystallises from the solution, on cooling, in long, four-sided prisms, and gradually evolves ammonia when exposed to the air. E. C. R.

**Estimation of the Heavy Metals by Titration with Sodium Sulphide.** By G. NEUMANN (*Monatsh.*, 1894, 15, 495—504).—The neutral solution of the metal to be estimated is first precipitated with a known excess of standard alkali sulphide, and the solution containing the suspended sulphide or hydroxide is rendered clear, if necessary, by the addition of sodium chloride solution. An aliquot part of the solution is then filtered off, or removed by means of a pipette, and the excess of sulphide indirectly determined in it; this is best done by boiling with a known excess of N/10 sulphuric acid and afterwards determining the unused acid by titration with N/10 potassium hydroxide. This indirect process is necessary, because the alkali sulphide destroys the colour of litmus and of phenolphthalein. The estimation of the amounts of metal in the following salts by this method gave excellent results:—alum, chrome alum, silver sulphate, copper sulphate, cobalt sulphate, cadmium sulphate, lead nitrate, manganese sulphate, nickel sulphate, ferrous sulphate, ferrous ammonium sulphate, ferric chloride. G. T. M.

**Colorimetric Estimation of Picric acid in its Compounds with Organic Bases.** By L. KUTUSOW (*Zeit. physiol. Chem.*, 1894, 20, 166—169).—Ptomaines are readily separated from mixtures by the addition of picric acid; the compound can be weighed, but the method here recommended is to estimate the picric acid colorimetrically, either by the spectrophotometer, or, more readily, by the use of Hoppe-Seyler's double pipette (Abstr., 1892, 1264). W. D. H.

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## General and Physical Chemistry.

**Refractometric Researches.** By J. F. EIJCKMAN (*Rec. Trav. Chim.*, 1894, **12**, 157—197).—In continuation of his refractometric observations (*Abstr.*, 1893. ii, 1), the author has measured the molecular refractions and dispersions of a large number of organic compounds. He finds generally that in any series of homologous compounds there is a regular change in both the refraction and dispersion with rising molecular weight if the higher members of the series are alone considered, but that this rule never holds for the initial members of the series. As a typical example the following series may be quoted.

	(A - 1)MV.	Difference for CH <sub>2</sub> .
Water .....	5.83	—
Methylic alcohol .....	12.93	7.10
Ethylic alcohol.....	20.54	7.61
Heptylic alcohol.....	58.39	5 × 7.57
Cetylic alcohol .....	126.76	9 × 7.59

The mean values obtained for the refraction of the CH<sub>2</sub> group from a large number of observations with different compounds, and using Gladstone's formula, are for the lines H<sub>α</sub>, H<sub>β</sub>, and for a ray of infinite wave-length A (calculated by means of Cauchy's formula)

$$\begin{aligned}\beta &= 7.889 \\ \alpha &= 7.754 \\ A &= 7.590,\end{aligned}$$

and for the dispersion  $\beta - \alpha = 0.1353$ .

The variations in the numbers actually obtained by observation from these mean values all lie within the limits allowable for error of experiment.

H. C.

**Optical Rotation of Ions.** By P. WALDEN (*Zeit. physikal. Chem.*, 1894, **15**, 196—208).—The author determined the optical rotation of solutions of  $\alpha$ -bromocamphosphulphonic acid and some of its salts, at various dilutions and constant temperature (20.5°), employing for the purpose the apparatus of Schmidt and Hänsch. In the case of the free acid, an increase in dilution from  $v = 2.08$  to  $v = 120$  was accompanied by a decrease in the molecular rotation of from 287° to 270°, so that the undissociated molecule possesses a somewhat greater rotatory power than the dissociated molecule. In the experiments with salts of lithium, sodium, potassium, beryllium, magnesium, zinc, and barium, dilution has in most cases a similar effect, whilst at equal dilution (also approximately equal dissociation) the molecular rotations were approximately equal as seen in the table.

<i>v.</i>	H.	Li.	Na.	K.	Tl.	Be.	Mg.	Zn.	Ba.
30 + 273°	275°	272°	273°	273°	274°	268°	272°	272°	
120 + 270	271	270	269	271	271	270	270	269	

The rotation is hence dependent on the number of active ions, and

at complete dissociation, in equimolecular solutions, the rotations of different salts containing the same active acid ion are equal.

In aqueous acetone solution (93 per cent. acetone), a much higher number ( $343^\circ$ ) was obtained at  $v = 30$ . The morphine and quinidine salts gave molecular rotations of  $-100^\circ$  and  $+1008^\circ$  respectively. The algebraic sum of the molecular rotations of the constituents being  $-100^\circ$  and  $+996^\circ$ ; the molecular rotation of an electrolyte of two active ions appears to be equal to the algebraic sum of their molecular rotations.

L. M. J.

**Development of the Latent Photographic Image by Alkali Peroxides.** By G. A. LE ROY (*Compt. rend.*, 119, 557).—Aqueous solutions of alkali peroxides, or a solution of hydrogen peroxide made strongly alkaline, can develop the latent image formed when emulsions of silver bromide or silver chloride in gelatin are exposed to light, the intensity of reduction being sensibly proportional to the quantity of light acting on the emulsion. The developing power of the alkali peroxides is, however, much below that of the substances usually employed as developers by photographers. The image, which consists of a mixture of metallic silver and silver oxides, is considerably reduced in intensity when placed in solutions of alkali thiosulphates or thiocyanates.

C. H. B.

**Light emitted during Crystallisation.** By E. BANDROWSK (*Zeit. physikal. Chem.*, 15, 323—326).—The author considers the light emitted during crystallisation to be in all probability electrical, and due to the union of electrified ions; for this reason, it should be most marked in the sudden crystallisation of strongly dissociated compounds, and the following experiments, suitable also for lecture purposes, are described. A glass cylinder is half filled with a warm saturated, sodium chloride solution, and into it is poured an equal quantity of hydrochloric acid sp. gr. 1.12, and the solutions mixed by a glass rod, when a bluish-green light fills the whole cylinder. Or the two liquids having been carefully poured in, the cylinder is strongly shaken, when a flash of light occurs. Alcohol may also be used in place of the acid, and similar effects may be obtained by the use of potassium chloride or bromide instead of the sodium salts. The former compound with alcohol gave a most marked effect, the light being stronger and greener than that obtained with sodium chloride.

L. M. J.

**Some Voltaic Combinations with a Fused Electrolyte and a Gaseous Depolariser.** By J. W. SWAN (*Proc. Roy. Soc.*, 1894, 56, 56—64).—The author describes a number of different cells of the Upward type, with a fused electrolyte and a gaseous depolariser. The electrolyte used was either the molten chlorides of sodium and potassium mixed, or chloride of lead. The cathode was always molten lead, and the anode carbon, chlorine being used as the depolariser. As a general conclusion, it was found that it is necessary that the surface of the carbon pole on which the cation is deposited be alternately exposed to the action of the gas and the electrolyte. The research proves that it is possible to form pyro-batteries of the Upward type,

although it is extremely difficult to realise the conditions required for effective action.

H. C.

**Polarisation. I. Solid Cathodes.** By J. ROSZKOWSKI (*Zeit. physikal. Chem.*, 1894, **15**, 267—304).—For the polarising E.M.F., the author employed a Gülich thermopile of 50 elements, capable of yielding a pressure up to 3·5 volts; a Leclanché cell, and four standard Clarke cells being employed for its determination. The cathode examined was immersed in a N/10 solution of sulphuric acid, and the polarisation determined by the measurement of the E.M.F. obtained from this cathode connected with a calomel element, that is, practically, the chain, cathode, N/10 sulphuric acid, potassium chloride solution, mercury. Experiments on the effect of the duration of the current were made with cathodes of polished and platinised platinum, polished silver and mercury, and the polarisation reached its maximum constant value in from two to three minutes (polished platinum 15 minutes). The effect of the current strength on the polarisation was obtained by the addition of external resistances. With a platinised platinum cathode of 2 square cm. area and an E.M.F. of 3·3 volts, the polarisation decreased to a minimum of -180 volts when 700 ohms had been added, further addition having no effect. A similar decrease was obtained by the addition of internal resistance, that is, substitution of Leclanché cells for the thermopile. The influence of the size of the cathode was investigated by the use of mercury electrodes of respectively 1 and 2 square cm., and although for low E.M.F.s the smaller cathode gave markedly greater polarisation, at 3·3 volts the values were almost identical. The nature of the surface was then altered and platinum electrodes (1) polished, (2) platinised, (3) platinised and heated to redness, (4) covered with scratches, were employed. Very different values for the polarisation were obtained, the highest values being obtained with (4) and lowest with (2). The platinised cathode also gave the curve of polarisation, polarising E.M.F., approximately a straight line of inclination  $\tan^{-1} \frac{1}{3}$ .

In no case does a maximum value occur, and the differences the author considers to be due to different occluding powers of the surfaces. Similar experiments were performed with silver cathodes with entirely similar results, the differences between the differently prepared silver cathodes being, however, not as great as with the platinum electrodes.

L. M. J.

**Polarisation. II. Liquid Cathodes.** By J. ROSZKOWSKI (*Zeit. physikal. Chem.*, 1894, **15**, 305—322; see preceding abstract).—Liquid cathodes consisting of mercury and amalgams of lead, zinc (1 per cent.) and copper (0·053 per cent.), were employed, and curves embodying the relations of polarisation to polarising force are given. In the cases of the zinc and lead amalgams, the curves are at first parallel to the axis of abscissæ, after which, like the other curves, they become approximately straight lines of inclination  $\tan^{-1} 0·62$ , and no indication of a maximum is apparent. A cathode of Wood's alloy was examined in both the solid and the liquid state,

the effect of increase of temperature being first determined by experiments on mercury. With an E.M.F. of above 3 volts the effect of temperature became constant, namely, an *increase* of polarisation of about 0.0003 volt per degree. In the experiments with Wood's alloy, no change in the polarisation was observed at the point of fusion or solidification. The curves obtained for both solid and liquid also were almost identical, and closely resembled those previously obtained, being at first parallel to the axis of abscissæ. Hence in this case the nature of the surface has but little effect on the polarisation, which, if the E.M.F. is above a certain value, is approximately a linear function of the polarising force.

L. M. J.

**Influence of Electrolytes on the Conductivity of Acetic acid.** By A. J. WAKEMAN (*Zeit. physikal. Chem.*, 1894, **15**, 159—182).—The conductivity was determined in the case of mixtures of acetic acid with varying quantities of cyanacetic, propionic, succinic, glycollic, and hydrochloric acids, and from the results the value of  $k$  was obtained. The conductivity was then calculated on the assumption that two solutions in which the concentration of the ions are equal do not alter on mixing, and hence that the effect of the addition of the solution of the second acid to the acetic acid solution may be regarded as (1) the abstraction of water from, or addition to, the latter until the two solutions become isohydric; (2) admixture of these isohydric solutions. The calculated values of the conductivity and of  $k$  obtained thus are compared with the observed values, and in most cases the agreement is very satisfactory. In the case of acetic and glycollic acids, concordance is only good when the former acid is in considerable excess. In all cases, as would be expected, the effect of strong acids is very much more marked than that of weak, the addition of  $\frac{1}{2000}$  cyanacetic or  $\frac{1}{1000}$  of hydrochloric acid being very noticeable. The conductivity of hydrogen chloride dissolved in acetic acid was also determined, but, owing to the great resistance, only with approximate accuracy. Curves expressing the results are also given.

L. M. J.

**Thermoelectric Properties of Salt Solutions.** By G. F. EMERY (*Proc. Roy. Soc.*, 1894, **55**, 356—373).—If a circuit is formed of two substances, one a metallic wire and the other a solution, and the junctions between the metal and the liquid are at different temperatures, an E.M.F. is developed in the circuit, which varies in magnitude nearly in proportion to the difference of temperature between the junctions, and, in comparison with the ordinary thermo-electromotive forces in metallic circuits, is very considerable. The author has made experiments to find out how the E.M.F. varies with variations both in the strength and in the nature of the solution. The results show that both have considerable influence on the magnitude of the E.M.F.

The E.M.F. per  $1^\circ$ , in terms of  $10^{-4}$  volt as unity,  $\theta$ , varies considerably with the concentration of the solution, and curves are plotted whose ordinates are equal to  $\theta$ , and abscissæ are the corresponding concentrations in gram molecules per litre of volume. For zero concentration, the curves all appear to start from somewhere about  $\theta = 8.6$  at an angle to the axes, and then, as concentration

increases, the curves bend round more or less sharply until they are nearly parallel to the axes of concentration. For some salts,  $\theta$  increases with increasing concentration, whilst for others it decreases, so that for thermoelectrical purposes we may divide salts into positive and negative, according as the value of  $\theta$  for the solution is greater or less than its apparent value for pure water. The final value for  $\theta$  in a solution appears to be due to the superposing of a salt effect on that due to the water itself.

A few experiments were made on the thermoelectric force generated in a purely liquid circuit, that is, in a circuit composed of two kinds of liquid, the junctions being at different temperatures. Experiments are also described, which lead to the conclusion that the thermoelectric forces at the junctions of metals and solutions are part of a system of reversible thermodynamic phenomena.

H. C.

**Method for Determining the Thermal Conductivity of Metals, with Applications to Copper, Silver, Gold, and Platinum.** By J. H. GRAY (*Proc. Roy. Soc.*, 1894, 56, 199—203).—One end of a given length of wire is kept at a constant known temperature. The rise of temperature of the other end of the wire is noted every minute, and, if proper precautions are taken to prevent loss by radiation from the sides, the data are obtained for calculating the thermal conductivity.

Several qualities of copper were tested, as well as pure gold, silver, and platinum. The values for the mean thermal conductivity in C.G.S. units, between the temperatures 10° and 97°, are given below.

	Conductivity.	Diameter.
Copper, Specimen 1.....	0.9594	2.00 mm.
"    "    2.....	0.88838	2.11 "
"    "    3.....	0.8612	3.09 "
"    "    4 (very impure)	0.3497	2.04 "
"    "    5 "    "	0.3198	2.04 "
Silver (pure) .....	0.9628	2.02 "
Gold " .....	0.7464	2.00 "
Platinum (pure) .....	0.1861	2.00 "

Experiments to find out if there is any relation between the electrical and thermal conductivities confirmed what has been found by previous investigators, that if one metal is a better conductor for heat it is also a better conductor for electricity. The results did not, however, prove that the ratios were always the same, although in some cases they agreed very closely.

H. C.

**Specific Heats of Gases at Constant Volume. Parts II and III. Carbonic Anhydride.** By J. JOLY (*Proc. Roy. Soc.*, 1894, 55, 390—391; 392—393).—The specific heat of carbonic anhydride at constant volume is given in terms of its variation with density  $\rho$ , for the mean specific heat between 12° and 100°, as

$$C_v = 0.1650 + 0.2125\rho + 0.3400\rho^2.$$

The following empirical equation expresses the line  $\rho = 0.124$ , calculated into a line of variation of specific heat with temperature.

$$C_v = a + 2b(100 - t) + 3c(100 - t)^2,$$

where  $t$  is the initial temperature of the experiment, and

$$a = 0.19020000$$

$$b = 0.00006750$$

$$c = 0.00000182$$

H. C.

**Law of Corresponding Boiling Points.** By G. W. A. KAHLBAUM and C. G. V. WIRKNER (*Ber.*, 1894, **27**, 3366—3374).—A reply to Dühring's criticism (this vol., ii, 37).

**Atomic and Molecular Solution Volumes.** By J. TRAUBE (*Ber.*, 1894, **27**, 3173—3178).—If  $m$  is the molecular weight of a substance dissolved in water,  $aq$  the amount of water which holds unit molecular weight of the substance in solution,  $d$  the density of the solution, and  $\delta$  the density of the water, the constant,

$$v_m = \frac{m + aq}{d} - \frac{aq}{\delta},$$

is called by the author the molecular solution volume, and the corresponding constant for the atom  $v_a$  the atomic solution volume. The densities of solutions of a number of compounds of some 50 elements have been determined, and a number of relationships between atomic and molecular solution volumes have been discovered. A summary of the chief results is given in this paper.

The elements hydrogen, lithium, sodium, silver, and univalent copper, gold, and silver have equal atomic solution volumes. In the series sodium, potassium, rubidium, and caesium, the atomic solution volumes increase by about 10 units with every rise in atomic weight. The atomic solution volume of rubidium is equal to that of ammonium. The thallium compounds have somewhat greater molecular solution volumes than the corresponding potassium compounds.

The elements calcium, strontium, and lead have equal atomic solution volumes, as have also the elements zinc and magnesium, barium and cadmium, bivalent iron and manganese, bivalent copper and nickel. Cobalt has a greater solution volume than nickel, and beryllium has the highest solution volume of any of the bivalent elements.

Equal solution volumes were also noticed in the following cases. Platinum, palladium, and iridium; aluminium and trivalent iron; molybdenum and tungsten in molybdates and tungstates; chlorine and bromine in chlorates and bromates; chlorine and manganese in perchlorates and permanganates; nitrogen and vanadium in nitrates and vanadates; carbon and silicon in carbonates and silicates.

The green chromium compounds have a smaller molecular solution volume than the violet. Iodates have a smaller solution volume than chlorates and bromates, but iodides have a greater volume than bromides, and bromides a greater volume than chlorides. The atomic solution volume of fluorine is smaller than that of chlorine. An increase in atomic solution volume with rising atomic weight is observed also in the series: oxygen, sulphur, selenium, tellurium; nitrogen, phosphorus, arsenic, antimony; silicon, titanium, zirconium.

The molecular solution volume is in every case an additive function. Water of crystallisation does not appear to be present in any of the dissolved salts. An atom may change its solution volume with change of valency. This property the author proposes to indicate by the term "polysterism." It follows from this property that there is a direct relationship between valency and atomic volume. H. C.

**The Critical State.** By K. WESENDONCK (*Zeit. physikal. Chem.*, 1894, **15**, 262—266).—The author describes some of the appearances observable in carbonic anhydride at the critical state, and points out that at  $31.7^{\circ}$  nebulosity is observable and inhomogeneity exists so that the true critical point must be higher than this; further researches are therefore desirable. L. M. J.

**Freezing Points of Concentrated Solutions.** By R. ABEGG (*Zeit. physikal. Chem.*, 1894, **15**, 209—260).—The lowering of the freezing point was first determined in aqueous solution at concentrations up to 5 gram molecules per litre; the compounds examined being chiefly the lower alcohols, acids, and ethereal salts. The osmotic work was calculated according to both Arrhenius' and Raoult's formulæ, and the results shown graphically against concentration as abscissæ. The curves are usually convex to the axis of abscissæ, and in those calculated according to Arrhenius' formula the inclination increases with the molecular weight, the Raoult curves being less divergent. The hydroxyl group usually tends to make the curve steeper, the reverse obtaining for the carboxyl group. A downward bending can be explained by the formation of aggregates, and this occurs with those compounds where Ramsay's and Shield's experiments indicated association. A number of ethereal salts were also examined in acetic acid and benzene solutions, and the results recorded graphically, whilst by interpolation the molecular osmotic work ( $\pi/n$ ) was obtained at a number of concentrations. Although the curves are not straight lines, a first approximation can be obtained by use of the formula  $\pi/n = A + Bn$ . In the case of mixtures, the osmotic pressure is greater than the sum of the osmotic pressures of the components separately, and this follows theoretically from the author's results, thus:  $\pi_1 = An_1 + Bn_1^2$ ,  $\pi_2 = An_2 + Bn_2^2$ ;  $\pi = A(n_1 + n_2) + \frac{B_1n_1 + B_2n_2}{n_1 + n_2} (n_1 + n_2)^2$ , that is,  $\pi = \pi_1 + \pi_2 + (B_1 + B_2)(n_1n_2)$ .

The osmotic pressures for mixtures of cane sugar and methylic alcohol, glycerol and ethylic alcohol, acetic acid and ethylic alcohol and glycerol and cane sugar in aqueous solutions were calculated, the values for A and B being obtained from the previous experiments. The agreement with the observed values was very satisfactory, and best for the calculations according to Raoult's method.

L. M. J.

**Solubility of Double Compounds.** By R. BEHREND (*Zeit. physikal. Chem.*, 1894, **15**, 183—195; see also Abstr., 1892, 1047, 1385).—The solubility relations of a mixture of picric acid and anthracene, which unite to form a double compound, were determined.



The compounds were purified as completely as possible, finely powdered, and added to 120 c.c. of 99.5 per cent. alcohol, the vessel being kept in circular motion at a temperature of 25° for eight days, after which quantities of the solution were withdrawn, and the constituents estimated. Eleven experiments are recorded; in the first, the solution was saturated with anthracene solely; in the last, with picric acid only; in the sixth, the anthracene picrate was first obtained in excess. The difference between the anthracene in the first and sixth experiments gave the quantity present in the latter as picrate, a similar calculation being possible for the picric acid from the sixth and twelfth experiments. The quantities of picrate so calculated were respectively 0.137 gram and 0.105 gram, and the mean value 0.121 gram was employed. The composition of the solution calculated thus is given in the following table.

Anthracene (total), $v$ ...	0.176	0.190	0.206	0.215	0.228	0.236
Picric acid (total) . . . . .	—	1.017	2.071	2.673	3.233	3.469
Anthracene (free), $u_1$ . . .	—	0.176	0.176	0.176	0.176	0.183
Picric acid (free), $u_2$ . . .	—	0.999	2.032	2.623	3.166	3.401
Picrate, $u$ . . . . .	—	0.632	0.069	0.089	0.119	0.121

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Anthracene (total), $v$ ...	0.202	0.180	0.162	0.151	0.149	—
Picric acid (total) . . . . .	3.994	5.087	5.843	6.727	7.511	7.452
Anthracene (free), $u_1$ . . .	0.149	0.127	0.109	0.098	0.096	—
Picric acid (free), $u_2$ . . .	3.926	5.019	5.775	6.659	7.443	—
Picrate, $u$ . . . . .	0.121	0.121	0.121	0.121	0.121	—

The values hence obtained for  $u_1 u_2 / u$ , vary only from 4.7 to 5.7, or within the experimental limits. L. M. J.

**Graphical Representation of Heterogeneous Systems.** By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, 1894, **15**, 145—158).—The author gives graphical representations of the equilibrium of systems consisting of from 1 to 4 substances. In the latter case, the edges of a regular tetrahedron are taken as axes, the coordinates of any point being measured parallel to sides of the figure. The influence of temperature and pressure must be expressed by a series of such tetrahedra. In the selection of the components, the following must be observed, (1) they should be the least possible; (2) they must be capable of entering into the system in varying proportions; (3) they must be in actual equilibrium under the conditions of the experiment. Substitution systems, as for instance  $\text{KCl} + \text{I} = \text{KI} + \text{Cl}$ , may be considered by deriving the equilibrium from that of the system of the three simple components. Similarly a double decomposition is obtainable from the tetrahedron of the four simple components, whilst a decomposition with apparently five components is also reducible to that of four. L. M. J.

**Principles of a New System of the Elements.** By J. TRAUBE (*Ber.*, 1894, **27**, 3179—3181).—The author has shown (this vol.,

ii, 70) that certain simple relationships exist between the atomic volumes of similar elements. In place of regarding the properties of the elements as functions of their atomic masses, he proposes an arrangement in which the atomic volumes are the determining factors. Similar elements then appear in groups having equal atomic volumes, or in which there are equal differences between the atomic volumes of allied elements.

H. C.

**Lecture Experiments: Ethyl Ether.** By F. BRANDSTÄTTER (*Chem. Centr.*, 1894, i, 1145—1146; from *Zeit. physikal.-Chem. Unterr.*, 7, 183—185).—The heaviness of ether vapour is easily shown by taking a small bottle half full of ether and closing it with a cork carrying two glass tubes; the one tube bent at right angles, and passing just through the cork, the other tube bent into an S-form, and having one end passing through the cork to just above the surface of the ether, the other and outside end being 6—8 cm. below the surface of the ether. The ether vapour will pass out of the lower end of this bent tube, and may be burnt. If two bottles, fitted in a similar way, are joined by a piece of rubber tubing, the size of the ether flame may be regulated by raising or lowering one of the bottles.

The lowering of temperature produced by the evaporation of ether is shown as follows. A strong test-tube is fitted with a cork carrying a thermometer and two glass tubes, the one reaching nearly to the bottom of the test-tube, the other just passing through the cork. The test-tube is charged with about 5 c.c. of water and 7 c.c. of ether, and a current of air passed through it. In a few minutes a temperature of  $-7^{\circ}$  to  $-8^{\circ}$  is obtained, and the liquid solidifies.

E. C. R.

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## Inorganic Chemistry.

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**Artificial Ice.** By A. C. CHRISTOMANOS (*Ber.*, 1894, **27**, 3431—3437).—Ice produced from the water supply of Athens was found to be separable into transparent and opaque portions. A detailed analysis showed very plainly that of these two varieties the former only was fit for consumption, being almost pure; the impurities of the original water were divided in various proportions between the opaque ice and the small amount of water that did not freeze.

M. O. F.

**Concentration and Distillation of Hydrogen Peroxide.** By R. WOLFFENSTEIN (*Ber.*, 1894, **27**, 3307—3312).—Hydrogen peroxide is relatively stable when heated, provided that the solution is free from alkaline compounds, from derivatives of the heavy metals, and from solids of every kind, even those that are chemically indifferent. Commercial hydrogen peroxide, 3 per cent., can be concentrated on the water bath in an ordinary dish at 75° until it contains 47·7 per cent. The yield is 61·8 per cent., the loss is due to volatilisation, and

not to decomposition, for, by the use of a beaker instead of a dish, the yield is 56 per cent. of solution, containing 64.7 per cent. of hydrogen peroxide. These solutions may be concentrated by distillation under reduced pressure, either directly or, preferably, after extraction with ether, to remove alumina. After repeated fractionation, almost pure (99.1 per cent.) hydrogen peroxide was obtained. It boils at 84–85° (68 mm.), is a colourless, syrupy liquid, does not readily moisten the containing vessel, is volatile in air, and irritates the skin, producing white marks which remain during several hours. It is strongly acid, and, when neutralised with alkali and distilled, the distillate readily reddens litmus. The preparation of large quantities of the pure peroxide is best accomplished by concentrating the commercial solution on the water bath until it contains about 20 per cent.; it is then evaporated under reduced pressure (68 mm.) until it contains 50–55 per cent., extracted with ether, and finally fractionated in a vacuum. The percentage of peroxide in the various solutions was determined by titration with potassium permanganate solution. The author is unable to confirm Schilow's statement, that a solution of peroxide containing 50 per cent. can be prepared by treating the commercial product (3 per cent.) with soda and extracting with ether.

The hydrates  $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$  have also been prepared; they are liquid at  $-20^\circ$ , but solidify in a mixture of solid carbonic anhydride and ether.

J. B. T.

**Bye-products formed from the interaction of Ozone and Ammonia.** By L. ILOSVAY DE NAGY ILOVA (*Ber.*, 1894, **27**, 3500–3503).—Carius, who has previously investigated this subject, found that ammonium nitrite and hydrogen peroxide were first produced, these then reacted further forming ammonium nitrate and water. The author gives a detailed account of his experiments, which are partly original and partly a repetition of Carius'. Ozone is readily absorbed by aqueous ammonia (2–20 per cent.) with formation of nitrite and nitrate. The action is more energetic as the concentration of the ammonia increases; whichever substance was in excess nitrate and nitrite were formed. Dry ozone and dry ammonia do not react at ordinary temperatures. Hydrogen peroxide could not be detected under any circumstances; the reagents employed for its recognition were titanium dioxide in concentrated sulphuric acid solution, and chromic anhydride and ether.

J. B. T.

**Formation of Hydrazine from Inorganic Compounds.** By P. DUDEN (*Ber.*, 1894, **27**, 3498–3499).—Hydrazine is formed by the reduction of recently-prepared potassium dinitrososulphonate,  $\text{K}_2\text{SO}_3\text{N}_2\text{O}_2$ , with sodium amalgam at  $0^\circ$ , and is separated by treatment with benzaldehyde. Zinc dust and ammonium hydroxide or soda may also be used as the reducing agent; other substances which act in alkaline solution cause the formation of hydroxylamine, ammonia, and potassium hyponitrite in varying quantity, and the yield of hydrazine is consequently much diminished.

J. B. T.

**Salts of Dinitrososulphonic acid.** By A. HANTZSCH (*Ber.*, 1894, 27, 3264—3273).—The author considers that the salts of this acid probably have the symmetrical formula  $O < \begin{smallmatrix} N \cdot OR \\ | \\ N \cdot SO_3R \end{smallmatrix}$  rather than the asymmetrical one  $NO \cdot N(OR) \cdot SO_3R$ , proposed by Raschig. Two isomeric potassium salts have been described. One of these gives a precipitate with barium chloride which is insoluble in water, but which dissolves in hydrochloric acid to form a solution which remains clear for a short time, but then deposits barium sulphate (Pelouze), whilst the other was only once obtained by Raschig, and gives no precipitate with barium chloride, although, on the addition of hydrochloric acid, an immediate precipitate of barium sulphate is formed. The author has succeeded in obtaining this second salt, but has been unable to prepare that described by Pelouze. Concentrated solutions of this salt give with barium chloride a precipitate of the *barium potassium salt*, which is soluble in a large amount of water. The *silver potassium salt* is a white mass, which decomposes at  $85^\circ$  with evolution of red fumes. A. H.

**Action of Hydrogen Phosphide on Potassammonium and Sodammonium.** By A. JOANNIS (*Compt. rend.*, 119, 557—559).—When hydrogen phosphide is passed into a solution of potassammonium in liquefied ammonia, the gas is absorbed and hydrogen is evolved, a liquid being formed which does not mix with the ammonia, although not quite insoluble in it. When the action is complete, and the excess of ammonia is allowed to volatilise, potassium hydrogen phosphide or potassium phosphine,  $PH_2K$ , is obtained in slender, white needles. When heated, it is converted into potassium phosphide,  $PK_3$ , with evolution of hydrogen phosphide, and water also decomposes it with evolution of hydrogen phosphide.

Sodammonium behaves similarly, the quantity of hydrogen liberated corresponding with the formation of the compound  $PH_2Na$ . The liquid solidifies when slowly cooled. If, however, the tube is kept at  $0^\circ$  and the ammonia is allowed to escape, a considerable quantity is retained by the phosphide, and the liquid does not solidify. No definite compound of the phosphide and ammonia seems to be formed, and a further quantity of the latter is evolved when the liquid is allowed to acquire the ordinary temperature. If it is heated at  $65^\circ$ , still more ammonia is liberated, and the residue solidifies, and has the composition  $PH_2Na$ . It decomposes in the same manner as the potassium compound.

When nitrous oxide is allowed to act on these derivatives of phosphine, a volume of nitrogen is liberated equal to the volume of nitrous oxide employed, and the action is therefore quite different from that between nitrous oxide and the amides. C. H. B.

**Crystallised Products formed in the Deacon Process.** By A. ARZRUNI and E. SCHÜTZ (*Zeit. Kryst. Min.*, 1894, 23, 529—535).—The authors give the results of the investigation of a series of crystallised products formed during the Deacon process of making chlorine, and presented to the collection of the Aix-la-Chapelle

Technical School by the director of the Rhenania Chemical Works at Stolberg. The following three compounds are described crystallographically and chemically.

1.  $\text{Cu}(\text{Fe}_2)_2\text{As}_4\text{O}_{17}$ , triclinic.
2.  $\text{Fe}_2(\text{AsO}_3)_2$ , monoclinic.
3.  $\text{Fe}_2(\text{AsO}_3)_2 + 10\text{H}_2\text{O}$ , rhombic.

B. H. B.

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## Mineralogical Chemistry.

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**Fresh Discoveries of Gypsum Crystals.** By G. STAATS (*Ber.*, 1894, 27, 3181—3182).—Fully-developed crystals were found near Crone on the Brahe (? in Posen), in a clay associated with lignite; the clay contained lime, magnesia, alumina, and iron. Swallow-tail twins were seldom found, but intersection twins were common.

C. F. B.

**Lindesite and Pyrrhoarsenite.** By L. J. IJELSTRÖM (*Zeit. Kryst. Min.*, 1894, 23, 590—593).—1. *Lindesite* is the name given to a new mineral found in the parish of Linde, Örebro, Sweden. The mineral is of a brownish-red colour, and has a hardness of about 6. Analysis gave the following results.

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
48·37	21·92	2·47	10·97	5·76	3·49	6·12	0·90	100·000

The formula is  $3\text{RO}, \text{SiO}_2, \text{R}_2\text{O}_3, \text{SiO}_2$ . The mineral consequently approaches acmite and rhodonite in composition.

2. *Pyrrhoarsenite*.—This mineral was discovered by the author in 1886, and analysed subsequently by A. G. Högbom. The author has now analysed it himself with the following results.

As <sub>2</sub> O <sub>3</sub> .	MnO.	FeO.	CaO.	MgO.	Total.
51·88	28·38	trace	15·55	3·33	99·14

B. H. B.

## Physiological Chemistry.

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**Influence of Intra-venous Injection of Dextrose on the Blood-gases.** By V. HARLEY (*Proc. Roy. Soc.*, 1894, 56, 148—154).—The experiments were made on dogs. Samples (30 c.c. in each) were collected before, an hour after, and 3—5 hours after the injection. There is a diminution in both carbonic anhydride and in oxygen after the injection. The lessening of carbonic anhydride supports the view that lactic acid derived from the sugar displaces the carbonic

anhydride in its combinations as sodium salt. The lessening of oxygen is very marked, and the explanation is not at present forthcoming.

W. D. H.

**Contents of the Healthy Stomach.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P., Edin.*, 1894, 5, 43—50; from *Edin. Med. J.*, 1893).—The following conclusions are drawn from the examination of the contents of the healthy stomach. (1) Free hydrochloric acid is secreted immediately the food enters; but this combines with proteid, so that salivary action is not impeded during this first stage. The free acid does not appear in the stomach contents till from half-an-hour to two or three hours after the meal is taken; the time varies according to the composition of the meal. Hydrochloric acid combined with proteid is less antiseptic than the free acid. The inorganic salts, especially the chlorides, and the total proteids per cent. in solution fall during the progress of digestion. Albumin (probably mucin, *sic*) increases, albumoses remain stationary, and peptone diminishes.

Physiological text-books are stated to be in error concerning the amount of acid; the following numbers are derived from the present observations.

Total acidity from . . . . .	0.108 to 0.36	per cent.
Combined acidity from ..	0.072 „ 0.324	„
Free acidity from . . . . .	0.018 „ 0.09	„

The causes of variation are the time after the ingestion of a meal and the character of the food taken. The free hydrochloric acid is seldom over 0.09 per cent. after a proteid meal, but it may rise to 0.162 or 0.27 after a meal chiefly carbohydrate in nature.

W. D. H.

**Analysis of Gastric Contents.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P., Edin.*, 1894, 5, 56—70; from *Internat. Med. Mag.*, October, 1893).—A description of certain methods for examining the gastric contents, with some modifications in the direction of simplifying them.

W. D. H.

**Action of Acids and Alkalis on the Gastric Secretion.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P., Edin.*, 1894, 5, 213—244).—An examination of the gastric contents after the administration of acids and alkalis in various forms of dyspepsia supports the well-known therapeutic doctrine that, if given before food, acids diminish and alkalis increase the acidity of the gastric juice.

W. D. H.

**Gastric Digestion of Proteids.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P., Edin.*, 1894, 5, 20—26; from *J. Anat. and Physiol.*, 27, 195).—The properties of the compounds formed between proteid matter and hydrochloric acid are in part described, and certain theoretical suggestions made concerning the mode of digestion of proteids in the stomach.

W. D. H.



**Influence of Fats on the Assimilation of Proteïds.** By R. LAAS (*Zeit. physiol. Chem.*, 1894, 20, 233—248).—The admixture of fat with proteïd food increases the nutritive value of the latter, more nitrogenous matter being assimilated. Fats, however, unlike carbohydrates, do not lessen the putrefactive changes in proteïd in the alimentary canal.  
W. D. H.

**Metabolism.** By I. MUNK (*Pflüger's Archiv*, 1894, 58, 309—408).—This is a series of five papers, all relating to various important points in connection with nutrition. The methods employed are as a rule similar to those generally used in metabolism experiments, and the experiments and results are discussed with great fulness. The first series of experiments, performed on dogs, show the great sparing influence on proteïds exerted by gelatin. In a mixed diet, fully five-sixths of the proteïd may be replaced by gelatin.

The second set of experiments relates to the loss of material during the condition of inanition in a dog. They take into account not only the loss of organic material, but also of the inorganic salts, and cannot be explained otherwise than that the bones share in the wasting as well as the softer tissues.

The third section discusses certain points of detail in connection with the sparing influence of carbohydrates on proteïds, with special reference to putrefactive changes, as evidenced by ethereal hydrogen sulphates in the urine.

The fourth discusses the influence on metabolism of the division of the food into rations, and leads to the important practical conclusion that in man the food should be divided into at least three meals in order to make the best use of the nutriment administered.

The fifth and last section treats of a variety of points, chiefly criticising certain recent researches. Among these, those of Hirschfeld and others stand especially prominent, in which it has been stated that a smaller nitrogenous intake is compatible with healthy equilibrium than was formerly supposed to be the case. This is a very important consideration, as diet tables for soldiers, convicts, &c., may have to be considerably altered with economical advantage if Hirschfeld is right. The present paper, however, lends no support to Hirschfeld's ideas. It is admitted that there are considerable personal variations from the normal standard (Voit: 118 grams proteïd, 36 grams fat, and 500 grams carbohydrate *per diem*). This normal must not be slavishly followed in individual cases, but expresses an average, from which, however, the variations after all are not very great; hence it should form the basis for the construction of average diets for large numbers of people.  
W. D. H.

**Influence of Carbonic Anhydride and Oxygen on Blood Coagulation.** By A. E. WRIGHT (*Proc. Roy. Soc.*, 1894, 55, 279—294).—The method used consisted in determining, by means of samples of blood withdrawn into capillary tubes, the alterations in the coagulability of the blood by altering the gaseous intake of living animals (dogs and rabbits). Increase of carbonic anhydride increases the rate of coagulation. The same is true for human blood in cases of

hæmophilia. Diminution of the carbonic anhydride decreases the coagulability to the original normal. Decrease and increase of oxygen cause respectively decrease and increase of coagulability.

W. D. H.

**Disappearance of Leucocytes from Blood after Peptone Injection.** By D. BRUCE (*Proc. Roy. Soc.*, 1894, **55**, 295—299).—Injection of peptone solution into the circulation of rabbits does not cause a destruction of leucocytes, but merely a withdrawal of them into various organs, notably the lungs and spleen.

W. D. H.

**Changes in Liver Cells.** By T. L. BRUNTON and S. DELÉPINE (*Proc. Roy. Soc.*, 1894, **55**, 424—438).—Various drugs were given to rabbits, and the effect on the liver cells noted. The compounds studied may be subdivided into three groups: (1) stimulating or excito-secretory, with pilocarpine for a type; (2) neutral; and (3) depresso-secretory, with atropine for a type. To the first group belong toluene, benzene, sodium iodide, pilocarpine, chrysophanic acid, ammonium chloride, metatolylenediamine, and nitric acid; to the second, aniline and phenol; to the third, phenol, atropine, and ammonia. The following caused marked increase in glycogen:—sodium iodide, metatolylenediamine, chrysophanic acid, toluene (?), ammonium chloride (?). The following did not do so, sometimes even causing a diminution of hepatic glycogen:—nitric acid, pilocarpine, benzene, and ammonium chloride (?). The following caused a marked diminution in the "free iron" in the liver:—sodium iodide, toluene, metatolylenediamine. The following caused a diminution of the "free iron," but in a less marked degree:—ammonium chloride, nitric acid, pilocarpine, benzene (in the fed liver); in the fasting liver, benzene causes a doubtful increase of iron. Ammonia causes a diminution of glycogen and an increase of iron. Atropine causes a slight diminution of glycogen and little change in the iron.

W. D. H.

**Chemical Stimulation of Sensory Nerves.** By P. GRÜTZNER (*Pflüger's Archiv*, 1894, **58**, 69—104).—It is well known from previous researches that the chemical stimulation of nervous structures produces different effects from other forms of stimulation. The present experiments confirm this statement, and are concerned with sensory nerves. The experiments fall into three categories—(1) on taste, (2) on reflex respiratory effects in animals, and (3) on pain in man. The chief results from the last of these three sets of experiments, which are given with greatest fulness, may be summarised as follows:—A wound in the finger having been made, solutions of various agents were applied to the exposed nerves, and the time at which pain was noticed, and the kind of pain experienced were noted. It was found that the pain reaction time for sodium iodide was 5, for an equivalent solution of sodium bromide 10, and of sodium chloride 50 seconds. The halogens themselves act in the reverse order, chlorine being the strongest stimulant. With potassium compounds, the chloride has the most, and the iodide the least intense action. Potassium hydroxide is stronger than sodium

hydroxide, and ammonia, which has no action on motor nerves, is stronger than either. Ammonium chloride acts more strongly than sodium chloride, which is nearly inactive, but rather less strongly than potassium chloride. Cæsium chloride is stronger still. Rubidium chloride acts about the same as potassium chloride. The chlorides of calcium, strontium, and barium show no great difference; all give a burning sensation, the chloride of calcium being strongest and quickest in its action. The chlorides of zinc, cadmium, and mercury act in the order named, but less strongly and less quickly than those of the alkaline earths.

With regard to acids, there was found a pretty constant agreement between the acidity or avidity of the acids and their physiological action on sensory nerves; nitric and hydrochloric acids coming first, then sulphuric, and then, at a long interval, phosphoric.

Of the monhydric alcohols the lowest act most feebly; the corresponding fatty acids act in the reverse direction. Glycerol, which is such a strong stimulus for motor nerves, has practically no action on sensory nerves.

W. D. H.

**Chemical Stimulation of Ciliated Epithelium.** By G. WEINLAND (*Pflüger's Archiv*, 1894, 58, 105—132).—Ciliated epithelium from the frog's oesophagus was used; it was examined microscopically in solutions of various substances. Sodium fluoride acts most harmfully; then in order of molecular weight and harmful action come the iodide, bromide, and chloride. The potassium compounds of the halogens act similarly, although in a less degree; they are stronger stimuli of nerves. Ammonium chloride acts more feebly than potassium chloride. The chlorides of potassium, rubidium, and cæsium arrange themselves in their harmful action in the order of their equivalent weights; the chlorides of calcium, strontium, and barium in the opposite order, the last named even stimulating ciliary activity.

Potassium chlorate is intensely more harmful than the chloride.

Of the halogens themselves, iodine is the most, and chlorine the least harmful.

The alkalis first stimulate then lessen ciliary activity; this is most marked with sodium hydroxide, then potassium hydroxide, ammonia coming last. Calcium, strontium, and barium hydroxides are stimulating, especially the first named.

Small equivalent quantities of acids heighten at first the activity of the epithelium, and then destroy it. In this direction phosphoric acid is weakest, then hydrochloric, and then sulphuric. The fatty acids act harmfully in the order of their molecular weights, except that formic acid acts more strongly than acetic.

On the whole, the action of these chemical substances is similar to their action on motor nerves.

W. D. H.

**Rennet and similar Ferments.** By R. PETERS (*Preisschrift, Rostock*, 1894).—By means of rennet, not only is the natural or artificial solution of caseinogen precipitable, but also solutions of casein, or boiled whey-proteid, and various other proteids of animal

and vegetable origin under certain conditions, of which the presence of calcium hydroxide is the most important. The precipitated proteid can be dissolved, and is again precipitable by the ferment. Part of the proteid, however, always remains in solution, due to splitting of the proteid molecule, as Hammarsten showed. Ferments similar in their action are found in different parts of the vegetable kingdom.

W. D. H.

**Colostrum of the Cow.** By L. VAUDIN (*J. Pharm.*, 1894, [5], 30, 337—339).—The following table gives the analytical results obtained:

	Just before calving.	Just after calving.				Five days after calving.
		1.	2.	3.	4.	
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Solids (dried at 95°) ....	27·615	24·49	27·356	22·47	24·17	14·37
Butter.....	1·30	6·32	3·84	1·36	2·42	5·18
Lactose.....	1·52	2·17	2·366	1·023	2·86	4·07
Ash (soluble).....	0·278	0·250	0·220	0·271	0·190	0·26
„ (insoluble).....	0·809	0·839	0·830	0·791	1·02	0·51
Calcium phosphate.....	0·622	0·630	0·660	0·605	0·87	0·38
Proteids.....	23·705	14·91	20·10	9·025	17·68	4·35
Acidity (as P <sub>2</sub> O <sub>5</sub> ).....	0·348	0·272	0·336	0·264	0·28	0·16

The lactose and butter are low before, and increase regularly after, calving. The ash or salts and proteids are very high before calving, decreasing afterwards, but the ratio between them changes. The composition of the salts also varies, sulphates being present during and immediately after parturition, but not in normal milk.

L. T. T.

**Albumoses in Serous Effusions.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P. Edin.*, 1894, 5, 51—55).—About 20 different kinds of dropsical fluid were examined, and albumoses were found in nearly every specimen, peptone in a few, in addition to the proteids usually described.

W. D. H.

*Note by Abstractor.*—These results are of but little value, as the albumin and globulin present were first removed by heat, an agency which would, of course, lead to the formation of these products of proteolysis.

**Ethylic Sulphide in Dog's Urine.** By J. J. ABEL (*Zeit. physiol. Chem.*, 1894, 20, 253—279).—Dog's urine, which has been treated with milk of lime or free alkalis, yields a volatile substance which is absorbed by concentrated sulphuric acid, from which it can be again liberated by neutralisation. It was identified as ethylic sulphide. The compound with mercuric chloride melts at 119°, not at 90° as formerly stated. With nitro-sulphuric acid, it gives a deep green coloration. On oxidation with potassium permanganate in strong sul-

phuric acid solution, ethylic sulphide yields acetic and sulphuric acids, and not the sulphone. W. D. H.

**Carbohydrates of Normal Urine.** By K. BAISCH (*Zeit. physiol. Chem.*, 1894, 20, 249—252; compare *Abstr.*, 1893, ii, 542; 1894, ii, 393).—The carbohydrates of normal urine are three in number: *d*-glucose, animal gum, and a third which in former communications was not identified. The present research shows that this is probably isomaltose, a substance formed during digestive processes; it agrees with isomaltose in the following properties: reduction of Fehling's solution, non-fermentability with yeast, dextro-rotation, crystalline form, solubilities and melting point of its osazone. W. D. H.

**Albuminuria.** By F. D. BOYD (*Rep. of Lab. R. C. P. Edin.*, 1894, 5, 79—84, 85—87, 88—102).—The total proteids were estimated by boiling, the albumin by boiling after removal of the globulin by half saturation with ammonium sulphate, the globulin by difference.

Both proteids are generally present; the proportion varies so much that it is not possible to diagnose the variety of kidney disease present by means of it. Even in amyloid degeneration, the globulin may not be in excess. In the albuminuria of pregnancy, the globulin is present in larger amount than in other forms of albuminuria. In the albuminuria of heart disease, the globulin is usually more abundant than in chronic interstitial nephritis. In acute nephritis, without hæmaturia, the two proteids are about equal; but when blood is present the globulin is proportionally more abundant.

Four cases of Bright's disease are recorded in which serum albumin was present, but serum globulin absent, or present only in the merest traces; and one case where globulin and albumoses were present, but albumin absent. In no case did the proteid quotient bear any relation to that of the blood. The amount of proteid is often greater than that found in transudations. From these considerations, the presence of proteid in the urine is considered to be due to secretion rather than transudation, and there is some evidence that the lower the state of nutrition of the renal epithelium the greater is the amount of globulin allowed to pass.

Some observations are recorded that confirm Posner's (*Virchow's Archiv*, 79, 318) observations. The urine secreted by the Malpighian tufts is by many physiologists regarded as albuminous. The albumin is considered to be re-absorbed as the urine passes along the renal tubules in the normal condition. Posner took pieces of the kidney and plunged them into boiling water for two or three minutes; sections were then prepared. Where albuminuria had been present, the microscope revealed coagulated masses of proteid in the capsule chambers and tubules, but when the healthy kidney, either of man or animals, was examined no such evidence of albumin was ever found. W. D. H.

**Hæmoglobinuria.** By A. L. GILLESPIE (*Rep. of Lab. R. C. P., Edin.*, 1894, 5, 192—198; from *Edin. Med. J.*, June, 1892).—Clinical details of a case of paroxysmal hæmoglobinuria are given; the chief

point of chemical interest is the observation that on one occasion the pigment present was not oxyhæmoglobin or methæmoglobin, as is usually the case, but acid hæmatin; or, at any rate, no reduction occurred on the addition of ammonium sulphide. The spectra of acid hæmatin and of methæmoglobin are, however, so similar that this evidence can hardly be regarded as conclusive since no measurements of the absorption bands are given.

W. D. H.

**Alcaptonuria.** By H. V. OGDEN (*Zeit. physiol. Chem.*, 1894, **20**, 280—286).—A case of this disease is described. It agrees in all important points with those previously described by Baumann, Wolkow, and Embden.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Dialysis of Beer Yeast.** By E. ONIMUS (*Compt. rend.*, 119, 479—480).—A solution of beer yeast in pure water, or in a solution of sugar, is allowed to diffuse through parchment-paper into a solution of sugar in boiled water; after 15 to 20 minutes, the sugar in the latter solution is inverted, although no cellules, but only some microzymes, can be detected in it. It is only after two or three hours that small, isolated yeast cellules are observed in the sugar solution, and only after 11 or 12 hours that chains of cells can be detected. It follows that beer yeast secretes a dialysable substance, and that inversion of the sugar takes place without actual contact with the yeast cells. The medium is first modified by the zymase, and only after this alteration constitutes a nidus favourable to the development of cells. C. H. B.

**Nitrifying Ferment.** By G. TOLOMEI (*Staz. Sper. Agrar.*, 1894, 26, 246—263).—After giving a short historical sketch of the subject of nitrification, the author describes his own experiments, which were mostly on the lines of those of previous investigators. It is concluded that nitrification is due to a micro-organism, that moisture is indispensable, that slight alkalinity is favourable, and that light, the chemically active rays, is prejudicial to the development of the organisms. Nitrification proceeds much more rapidly in porous than in compact substances, and is assisted by small quantities of ozone. Variations of temperature hinder nitrification. N. H. J. M.

**Glutamine in the Green Parts of Plants.** By E. SCHULZE (*Zeit. physiol. Chem.*, 1894, 20, 327—334).—It has been previously shown that in the families Caryophyllaceæ and Filices no asparagine is found. It was therefore expected that glutamine occurred instead. The correctness of this hypothesis is shown by the experiments recorded in the present paper; further experiments show that glutamine is formed in the leaves. W. D. H.

**Crystalline Nitrogenous Compounds in Seedlings.** By E. SCHULZE (*Zeit. physiol. Chem.*, 1894, **20**, 306—326).—This is mainly a review of previous work. Different seedlings yield to analytical processes different nitrogenous crystalline products. Thus, in *Lupinus luteus*, asparagine, phenylalanine, amidovaleric acid, arginine, choline, and xanthine-like substances are found; in *Cucurbita pepo*, glutamine, asparagine, leucine, tyrosine, arginine, choline, vernine, and xanthine-like substances; in *Vicia sativa*, asparagine, phenylalanine, leucine, amidovaleric acid, guanidine, choline, and betaine. This does not indicate that in plant metabolism the proteid molecule breaks down in different ways, it being contended that the disintegrative metabolism of proteid is qualitatively the same, but varies quantitatively. This is supported by experiments on plants of the same kind, only of different ages. It may also be that in some plants certain varieties of nitrogenous crystalline compounds are used more in nourishing the tissues, whilst in other plants other compounds are more advantageous, and so are used up first.

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W. D. H.



## Analytical Chemistry.

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**Thioacetic acid as a Substitute for Hydrogen Sulphide in Qualitative Analysis.** By R. SCHIFF and N. P. TARUGI (*Ber.*, 1894, 27, 3437—3439).—Excellent results may be obtained by employing thioacetic acid instead of a current of hydrogen sulphide in qualitative analysis. About 2 c.c. of a 30 per cent. solution of ammonium thioacetate is simply added to the solution, made acid with hydrochloric acid in the usual way, and the liquid boiled. The reactions given by the metals appear to be identical with those obtained with hydrogen sulphide, but the time required for precipitation is greatly lessened. The only products of decomposition of the acid in the presence of hydrochloric acid are ammonium chloride, acetic acid, and hydrogen sulphide, so that the separation of the metals remaining unprecipitated is not interfered with. The reagent has been used for some time, and with great success, in the laboratories of the University of Pisa. A. H.

**New Applications of Alkalimetry and Acidimetry.** By F. HUNDESHAGEN (*Chem. Zeit.*, 1894, 18, 505—506, 547).—*Estimation of the Hardness of Water.*—The reagents wanted are a solution of 3.786 grams of sodium carbonate in 1 litre of water and dilute nitric or hydrochloric acid of corresponding strength. 200 c.c. of the sample is titrated directly with this acid, tincture of cochinnelle serving as indicator. Each c.c. of acid shows 1° of temporary hardness (German scale). The permanent hardness is estimated as follows. 200 c.c. of the sample is mixed with a moderate excess of the sodium carbonate solution, evaporated to dryness, and the residue, after being moistened with a little water, is once more evaporated and heated to about 200°. It is now dissolved in a little water, the liquid

filtered, and the insoluble matter washed with about 50 c.c. of water. The filtrate is then titrated as before. The number of c.c. of acid deducted from the c.c. of added soda represents the permanent hardness. The total hardness may be estimated directly by using the resulting liquid from the estimation of the temporary hardness for the determination of the permanent hardness.

*Volumetric Estimation of Phosphoric acid by Titrating the Yellow Precipitate.*—The liquid should not contain more than 0.05 gram of phosphoric anhydride. If free hydrochloric or sulphuric acid is present, the phosphate is precipitated with a little ammonia and at once redissolved in nitric acid. After adding some ammonium nitrate and a little ammonium sulphate, the liquid is heated, precipitated with a slight excess of molybdate solution, and the precipitate collected and washed with a 1 per cent. solution of potassium nitrate, until the filtrate is practically neutral. The filter is then put back into the beaker, from 10 to 50 c.c. of water is added, and, after adding a few drops of 1 per cent. solution of phenolphthalein, the mixture is titrated with normal alkali until the precipitate has all dissolved, and the liquid turned permanently red. It is advisable to add a slight excess of the alkali, and then to titrate back with normal acid. 1 c.c. of normal alkali = 0.003077 gram of phosphoric anhydride.

*Acidimetric Estimation of Tungstic acid.*—The acid is separated in the usual manner, without troubling about any silica which may be present. The precipitate, after being washed, first by decantation, and then on the filter, with a 5–10 per cent. solution of potassium nitrate, is mixed with water, heated to boiling, and dissolved in excess of normal soda. The excess of alkali is titrated back with normal acid, phenolphthalein serving as indicator; 1 c.c. of normal alkali = 0.116 gram of tungstic anhydride.

L. DE K.

**Estimation of small Quantities of Chlorine in Fats.** By R. BENEDIKT and H. ZIKES (*Chem. Zeit.*, 1894, 18, 640–641).—A tube, made of hard glass, 100–110 cm. long and 11–12 mm. wide, is drawn out funnel shaped at one end and bent at an angle of 45° upwards. The funnel is provided with a doubly perforated india-rubber cork, through which passes a narrow bent tube for admitting air or carbonic anhydride, whilst the other hole admits a tube connected with a calibrated 100 c.c. reservoir containing the oil. The tube is made ready for use by introducing in the middle two separate 15–20 cm. layers of lime held together by plugs of asbestos. The empty space between the bend and the first plug of asbestos is filled up with broken pieces of porcelain. The tube is now laid in the combustion furnace, which must extend slightly beyond the second layer of lime. The other opening is closed with a cork through which passes a bent tube connected with a test-tube to collect any tar; another narrow tube carries off the gases, which must be lighted, and which indicate the progress of the combustion.

When the lime is red hot, the oil is very slowly admitted, a very slow current of carbonic anhydride being also passed through. When, after 3 to 5 hours, about 25–30 grams of oil has entered the tube, the supply is stopped, and, when the flame has gone out, the tube is

allowed to cool; it is then emptied, and the contents examined for chlorine in the usual manner. The test analyses are very satisfactory.

L. DE K.

**Estimation of Organic Nitrogen by Stock's Method.** By C. E. ZAY (*Staz. Sper. Agrar.*, 1894, 26, 22—31).—The nitrogen of several substances was determined by Kjeldahl's method (employing 20 c.c. of sulphuric acid containing 200 grams of phosphoric anhydride per litre) and by Stock's modification—using manganese dioxide (5 grams) with (1) sulphuric acid alone, and (2) with sulphuric acid containing phosphoric anhydride (20 c.c. per litre). Concordant results were obtained, and the employment of manganese dioxide effected a very great saving of time in the decomposition process.

N. H. J. M.

**Volumetric Estimation of Nitric acid.** By D. MONNIER and H. AURIOL (*Chem. Centr.*, 1894, 24, 1095—1096; from *Arch. sci. phys.*, Genève, 31, 352—358).—The process is based on the well-known principle that nitrates are reduced by nascent hydrogen. Sodium amalgam, prepared by adding 1 part of sodium to 100 parts of hot mercury, is allowed to act on the solution of the nitrate in the presence of tartaric acid. The hydrogen is collected and measured, and a check experiment is made with the same amount of amalgam without the nitrate. The difference of hydrogen evolved is the measure for calculating the amount of nitric acid.

L. DE K.

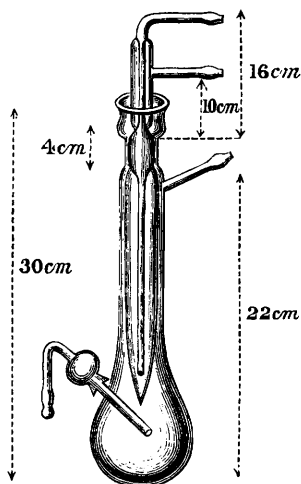
**Genuineness of Basic Slag.** By F. SESTINI (*Staz. Sper. Agrar.*, 1894, 26, 57—62).—Some samples of slag which the author had occasion to examine contained about 16 per cent. of total phosphoric anhydride and 4.4 to 5.8 per cent. soluble in dilute acetic acid (1 : 2), whilst the sp. gr., the amounts of water and of lime were about the same as are found in the case of normal slag. The results obtained indicate that the small amount of soluble phosphoric acid is not due to adulteration, but is connected with the amounts of ferric and ferrous oxide and alumina (about 3 per cent.) soluble in the same dilute acetic acid.

After discussing Wrampelmeyer's methods for the examination of basic slag (*Abstr.*, 1894, ii, 119), the author points out that it is sometimes more difficult than was supposed to distinguish between an adulterated slag and one which owes its sparing solubility to its mode of production. The amount of ferrous oxide which a slag contains is of interest, as it does not occur in natural phosphates, and the different portions which can be separated from each other by levigation should be examined.

N. H. J. M.

**Estimation of Carbon in Steel.** By H. KOCH (*Chem. Zeit.*, 1894, 18, 485).—Air contained in a gasometer is first passed through a washbottle filled with sulphuric acid, then through two bottles containing solid potash; then comes an empty bottle, and, finally, one filled with sulphuric acid. The purified air then passes through the lower tube of the combustion flask, where it removes the carbonic anhydride and any hydrocarbons formed during the process, and

it escapes through the upper tube. The gases are dried in a calcium chloride tube and completely burnt by passing them through a combustion tube containing red hot copper oxide. The resulting carbonic anhydride is first dried by passing it over calcium chloride and phosphoric anhydride, and then absorbed in a weighed potash apparatus to which is sealed a tube containing phosphoric anhydride. When required for the analysis of steel, the apparatus and combustion tube must first be completely freed from any carbonic acid or carbonaceous matter; the copper oxide is therefore heated to redness, a current of purified air being transmitted for some time. Into the flask is introduced 8 grams of chromic acid and 120 c.c. of dilute sulphuric acid (4 : 3) and the mixture boiled out. Afterwards 2 grams of the steel borings are introduced into the flask, the apparatus is connected with the combustion tube, and the operation conducted as usual. It will be noticed that the apparatus consists of two essential parts, the flask proper and a cooling contrivance.



Height of flask, 30 cm.  
Contents, 250 c.c.  
Width of ground neck, 4 cm.

L. DE K.

**Sodium Cobalt Nitrite as a Reagent for Potassium.** By J. VAN EYK (*Chem. Centr.*, 1894, i, 1162; from *Nederl. Tijdsch. Pharm.*, 6, 136—139).—The sodium cobalt nitrite is prepared by adding 100 c.c. of a 60 per cent. solution of sodium nitrite to a solution of cobalt nitrate (30 grams) in water (60 grams). After the evolution of nitric oxide has ceased, the mixture is filtered, and the salt precipitated with alcohol. By means of this salt, potassium can be detected when diluted to the extent of 1 : 10000. Ammonium salts are also precipitated by the reagent, but not until the concentration reaches 1 in 2000.

E. C. R.

**Assay of Nitre.** By A. HELLICH (*Chem. Zeit.*, 1894, 18, 485—486).—The author has noticed that commercial nitre often contains perceptible quantities of perchlorates, and consequently should be tested for this impurity. Its presence, which is difficult to account for, has until now been ignored in the various schemes for nitre analysis.

L. DE K.

**Estimation of Mercury in the Presence of Iodine.** By FRANÇOIS (*J. Pharm.*, 1894, [5], 30, 249—254).—The estimation of mercury when combined in any form with iodine is easily effected by electrolysis. The salt need not be dissolved, but merely placed in the

electrolysing vessel with the electrolyte. The latter may be dilute sulphuric acid, but the author finds the best electrolyte for this purpose to be formed by dissolving 20 grams of pure ammonium nitrate in concentrated pure ammonia, and making up with the latter to 100 c.c. The electrolysis is carried out in a platinum crucible of which the bottom is connected with the negative pole of the battery (two Bunsen cells). The positive pole is formed by a platinum rod, of which only about 1 mm. dips into the liquid. The mercury is deposited on the bottom of the crucible. When the action is finished, the solution is removed with a pipette, and the mercury is washed first with water and finally with alcohol, dried, and weighed with the crucible. The iodine in the solution is reduced with sulphurous acid, and estimated as silver iodide. This process may also be used for estimating mercury in the presence of bromine or chlorine.

L. T. T.

**Qualitative Separation of Chromium from Iron and Aluminium.** By R. B. RIGGS (*Amer. J. Sci.*, 1894, **287**, 409—411).—The mixed hydroxides or basic acetates containing about 0.1 gram of each metal are digested in 100 c.c. of water to which 10 c.c. of hydrogen peroxide and 1 gram of sodium hydroxide has been added, until effervescence ceases. After filtering off the iron, the liquid is slightly acidified with acetic acid, and the aluminium precipitated by ammonia. If the filtrate is yellow, this is a sure sign of the presence of chromium, which may, however, be confirmed, for instance, by the well-known hydrogen peroxide test.

L. DE K.

**Apparatus for the Assay of Pyrolusite by Bunsen's Process.** By C. ULLMANN (*Chem. Zeit.*, 1894, **18**, 487).—A beaker filled with the requisite amount of solution of potassium iodide is placed on a block of wood of about the same height. In the beaker is placed a special apparatus to collect the chlorine, a kind of upright glass condenser, the inner tube of which is drawn out like a pipette, and the top of which is provided with a stopcock and funnel. The tube is filled by drawing out the air through the funnel and then closing the stopcock. The flask containing the sample and a sufficiency of hydrochloric acid is now connected with a doubly-bent delivery tube provided with a bulb. Heat is applied, and after the bulk of the air has collected in the apparatus, the chlorine enters, and is, of course, rapidly absorbed by the potassium iodide. When all the chlorine has been boiled off, the stopcock is opened, and the beaker is placed on the table. After rinsing the apparatus and delivering tube, the liberated iodine is titrated as usual with thiosulphate.

L. DE K.

**Standardising Potassium Permanganate.** By Miss C. F. ROBERTS (*Amer. J. Sci.*, 1894, **286**, 290—292).—The author recommends standardising potassium permanganate by means of a solution of ferrous chloride, made by dissolving a known quantity of electrolytically-prepared metallic iron.

About 10 grams of iron ammonium sulphate is dissolved in 150 c.c.

of water, 5 c.c. of a saturated solution of potassium oxalate is added, and the whole is then heated with a sufficiency of ammonium oxalate until a clear solution is obtained. This solution is then decomposed in a beaker between two platinum electrodes, the iron being deposited on a weighed piece of platinum foil of a size convenient to be inserted in a rather large weighing bottle. After about  $1\frac{1}{2}$  hours with a current of 2 ampères, a sufficient amount of metal will have precipitated, when it is washed and dried in the usual way. L. DE K.

**Estimation of Iron in the Ash of Vegetable or Animal Matter.** By M. RIPPER (*Chem. Zeit.*, 1894, 18, 133—134).—The ash is dissolved in strong hydrochloric acid, the solution mixed with a few c.c. of hydrogen peroxide, and evaporated to dryness on the water bath; the residue is then just moistened with a few drops of hydrochloric acid, dissolved in about 20 c.c. of water, and transferred to a beaker. About 1.5 grams of potassium iodide is added, the beaker covered with a watch glass, and heated for 10 minutes at  $60^{\circ}$ ; the liberated iodine is then titrated in the usual manner with N/100 sodium thio-sulphate.

The process, which hitherto has only been used for the estimation of fairly large quantities of iron, only occupies one or two hours, and compares favourably with the gravimetric methods. L. DE K.

**Electrolytic Separation of Iron and Cobalt from Zinc.** By G. VORTMANN (*Chem. Centr.*, 1894, i, 877; see Abstr., 1894, ii, 34).—In separating iron from zinc by the electrolysis of an alkaline tartrate solution, only a single accumulator, giving a current of 0.07—0.1 ampère, should be used instead of the two formerly recommended; it then becomes unnecessary to redissolve the iron, since it is deposited free from zinc. The electrolysis should be commenced in the cold, but towards the end a temperature of  $50$ — $60^{\circ}$  promotes the deposition. The cathode (a disc of platinum, silver, or silvered copper, 50 mm. in diameter) should be from time to time replaced by a new one, and the operation continued as long as any gain in weight takes place. After the removal of the iron from the solution, the zinc is deposited by using two accumulators in series, with an E.M.F. of 4 volts.

Cobalt is also better separated from zinc in an alkaline tartrate solution by using 2 volts than by 4. Addition of potassium iodide diminishes the deposition of cobaltic oxide on the anode, but as this cannot be completely prevented the anode must likewise be weighed. The operation is performed as for iron, but with a warm solution.

M. J. S.

**Separation of Arsenic, Tin, or Antimony from Lead, Copper, Silver, Cadmium, Cobalt, Nickel, &c.** By P. JANNASCH (*Ber.*, 1894, 27, 3335—3336).—Elements, such as arsenic and tin, the chlorides of which are comparatively volatile, may be separated from other metals by dissolving the mixture in nitric acid or aqua regia in a special glass vessel, evaporating, and heating the residue at a suitable temperature in a current of dry hydrogen chloride, the vessel being placed in a nickel air bath, which can be heated up to  $450^{\circ}$ ;

the more volatile chlorides distil over, and are collected. Details of the apparatus were given in a previous paper (Abstr., 1894, ii, 330).

C. F. B.

**Action of Organic Matters on Potassium Permanganate.** By A. ZEGA (*Chem. Zeit.*, 1894, 18, 2—3).—The author has proved that trustworthy, comparable results in the titration of organic matters contained in potable waters may be obtained by operating in the following manner.

50 c.c. of the sample is put into a 100 c.c. flask, mixed with 5 c.c. of the usual permanganate solution, 5 c.c. of dilute sulphuric acid (1 : 2) added, and the mixture heated for 20 minutes on a water bath; the excess of permanganate is then titrated back by oxalic acid. The process is particularly useful when the water contains volatile organic matters. The standard permanganate is checked under the same conditions.

L. DE K.

**Analysis of Petroleums.** By A. RICHE and G. HALPHEN (*J. Pharm.*, 1894, [5], 30, 289—300).—The object of this work was to find methods for distinguishing (*a*) between petroleums of Russian and American origin, and (*b*) between crude oils, and mixtures of refined and residual oils. As a rule, the Russian oils contain less volatile oils and are denser than the American; for fractions of the same boiling point, Russian oils are generally denser than American, the mean sp. gr. of the fraction 140—160°, for example, being, for Russian oils 0.782, and for American 0.755. The refractive indices vary directly with the sp. gr., and so for fractions of the same boiling point are higher for Russian than for American oils. Russian oils are generally poorer in light oils and richer in heavy oils than American, whilst the latter are richer in solid paraffins, and are often rendered turbid by cold from separation of these substances. The American petroleums are generally almost exclusively composed of saturated hydrocarbons, whilst the heavier portions of the Russian oils generally contain hydrocarbons of the  $C_nH_{2n}$  series. None of these differences are, however, sufficiently certain to form satisfactory bases for analysis.

The authors have found the best test to be the solubility of the oils in a mixture of equal volumes of chloroform and alcohol. 4 grams of the refined petroleum to be tested (of which the density at 15° has already been determined) is introduced into a flask, and the alcohol-chloroform mixture gradually added from a burette until the liquid, which is at first rendered turbid, again becomes clear; the quantity of solution required is then noted. The fractions chosen should be those of about sp. gr. 0.800 to 0.830, as at these densities the difference is most marked. Thus, for sp. gr. 0.820 American refined oils required from 8 to 11 c.c. of the alcohol-chloroform for solution, the mean being 9.5 c.c., whilst for Russian oils the numbers were 4.3 to 4.8 c.c., giving a mean of 4.5 c.c.

For crude oils, a much larger amount of solvent is required; Russian crude oils of sp. gr. 0.851 to 0.877 requiring about 15 c.c., whilst refined oils of the same sp. gr. or mixtures of refined oils with about 10 per cent. of residuals, only required from 4 to 5 c.c. With

American crude oils, of which the sp. gr. varies from 0.788 to 0.822, the solvent required also amounts to about 15 c.c., whilst with the same oils refined, or mixtures of refined with residuals, from 5 to 7 c.c. only are required. A few of the very light American crude oils (of about 0.785 sp. gr.) require much less of the solvent.

Full tables and curves of solubility are given in the paper, and a special form of burette for keeping the alcohol-chloroform out of contact with the air is described.

L. T. T.

**Assay of Ethereal Oils.** By J. KLIMONT (*Chem. Zeit.*, 1894, 18, 641—642; 672—673).—The author's process is based on the fact that ethereal oils react strongly with bromine, whilst paraffin oil gives scarcely any reaction. For the assay of oil of turpentine, for instance, the following reagents are required. Solution of bromine in chloroform of about 1 per cent. strength; pure chloroform, treated with strong sulphuric acid, washed, and redistilled; pure turpentine, made by first washing oil of turpentine with aqueous soda, and afterwards collecting the fraction distilling over at 168—170°. 0.5 c.c. of this is put into a stoppered 20 c.c. flask and accurately weighed; chloroform is then poured in up to the mark, and the solution put into a little burette. 10 c.c. of the bromine solution is introduced into another little flask, and the turpentine solution slowly added until the colour of the bromine has entirely disappeared. If now a suspected sample of turpentine is at once treated in the same way as the pure specimen, its lesser bromine-decolorising power will indicate a more or less marked adulteration.

The author has tabulated the results of experiments with almost every known ethereal oil, including 9 specimens of refined turpentine and 11 of inferior brands; also experiments with adulterants, such as resin oil and petroleum. The figures given are not bromine numbers, but represent the equivalent amount of turpentine.

L. DE K.

**Detection of Methylated Spirit in Tinctures, &c.** By A. ASHBY (*Analyst*, 19, 261—271).—The author has satisfied himself that, of the numerous methods proposed, the test with sodium nitroprusside in the presence of ammonia is the best. The red colour will appear within 10 or 15 minutes. The constituent the reaction is chiefly due to has yet to be ascertained.

When examining alcoholic liquids free from solid matter, the test may be applied directly by mixing the sample with an equal bulk of a 1 per cent. solution of sodium nitroprusside and adding a few drops of ammonia; but in the case of official tinctures, 25 c.c. of the sample is distilled, and the first 5 c.c. which pass over tested. Ethereal solutions are distilled to dryness, and successive portions of the distillate are tested; if, however, the sample is very weak in spirit, it is best to add 2 or 3 c.c. of strong, pure alcohol to the distillate before applying the test. If the not very probable presence of a sulphide be suspected, it is best to add some fixed alkali before distilling.

L. DE K.

**Gravimetric Estimation of Sugar by means of Alkaline Copper Solutions.** By L. GRÜNHUT (*Chem. Zeit.*, 1894, 18, 447—



448).—Owing to the great difficulty of completely oxidising cuprous oxide, the results obtained by weighing the copper oxide are often much too low; weighing as cuprous oxide on a filter has also its disadvantages.

The author strongly recommends the process wherein the cuprous oxide is collected on a weighed asbestos filter contained in a glass tube. After first igniting in a current of air to burn off organic matters, the oxide is reduced in a current of dry hydrogen and the residual metal finally weighed.

L. DE K.

**Gravimetric Estimation of Glucose.** By F. GAUD (*Compt. rend.*, 119, 478—479).—50 c.c. of the freshly-prepared alkaline copper solution is mixed with an equal volume of water, boiled for a few minutes in a porcelain dish, and then placed on a water bath, the water in which is boiling; 25 c.c. of the sugar solution, containing about 1 per cent. of glucose, is then added all at once. Reduction under these circumstances takes place below 100°, a condition which is essential to prevent the destructive action of the alkali on the glucose. After 10 minutes, reduction being complete, the liquid, which should have a deep blue colour, is decanted off, and the precipitate is washed with boiled water until the washings are no longer alkaline to phenolphthaleïn. The precipitate is then transferred to a sp. gr. bottle holding 20 to 25 c.c., the capacity of which at 0° is known, and the bottle is filled up to the mark with boiled water and weighed at a temperature  $t$ .

Let  $P$  be the weight of the liquid and precipitate, the total volume of which is equal to the capacity of the flask at the temperature  $t$ , that is to say,  $V_t = V_0[1 + 3\beta(t - t_0)]$ . The sp. gr. of dried cuprous oxide is  $\Delta = 5.881$ , and the sp. gr.,  $d$ , of water at the temperature  $t$  is known; then the weight  $p$  of cuprous oxide is given by the expression

$$p = \frac{P - V_t d}{1 - d/\Delta}.$$

To obtain perfect results, the weight  $P$  should be reduced to a vacuum. The change in the sp. gr. of cuprous oxide caused by ordinary changes of temperature is too small to affect the result.

The weight of cuprous oxide is not strictly proportional to the weight of glucose present, and it is necessary to prepare a table showing the relation between various values of the two numbers. The author obtained the following results.

Cuprous oxide. Milligrams.	Glucose. Milligrams.	Cuprous oxide. Milligrams.	Glucose. Milligrams.
10	5.413	100	46.22
20	9.761	200	91.047
30	14.197	300	138.842
50	23.036	400	188.928

C. H. B.

**Modification of the Copper Test for Glucose.** By ALLEIN and F. GAUD (*J. Pharm.*, 1894, [5], 30, 305—307).—The authors find

(this vol., i, 123) that the free potash or soda in Fehling solution causes the decomposition of a part of the glucose to be estimated, and thus causes the low results known to be obtained by that method. The following solution gives results free from this error. 8.7916 grams of pure (electrically deposited) copper is dissolved in 93 grams of sulphuric acid, the solution is diluted with its own volume of water, and the whole made up to 1000 c.c. with strong ammonia. A deep blue solution is thus obtained, which is perfectly stable, and of which 10 c.c. corresponds with 0.05 gram of glucose. The estimation is conducted in a flask fitted with a triple-bored cork to admit the end of the burette containing the glucose solution and tubes for passing a current of hydrogen. 10 c.c. of the ammonio-copper solution and 10 c.c. of ammonia are introduced into the flask on a water bath, and heated to about 80°, and the liquid containing the glucose is then added drop by drop until the solution becomes colourless. If desired, the solution may be reoxidised (by substituting a stream of air for that of hydrogen as long as the reproduced blue colour deepens) and a second estimation be then performed. The cuprous oxide dissolving in the ammonia to a clear, colourless solution, renders the end of the reaction very sharp and exact.

L. T. T.

*Note.*—No reference is made to the earlier processes of Pavy and others, in which ammoniacal copper solutions are employed.—EDITORS.

**Estimation of Crystallisable Sugar in Raw Sugars.** By M. KARCZ (*Chem. Centr.*, 1894, 17, 845—846; from *Zeit. Zuck. Ind.*, 23, 21—24).—Thirty or fifty grams of the sample is mixed in a dish with an equal weight of absolute glycerol, and placed for some time in a desiccator. The glycerol soon dissolves the adhering syrup, but leaves the crystals intact. After pouring the glycerol into a glass funnel filled with cotton wool, and provided with a cover containing a calcium chloride tube, an aliquot part of the filtrate is examined in the polariscope. The polarisation deducted from that of the original raw sugar gives the amount of crystallisable cane sugar in the sample.

L. DE K.

**Estimation of Cane Sugar in Beer Wort.** By K. AMTHOR (*Chem. Centr.*, 1894, i, 932—933; from *Zeit. Nahrungsmittelunters. Hygiene*, 8, 80—81).—A criticism of Jais' process (*Abstr.*, 1894, ii, 123). Whereas Jais, in estimating the maltose and inverted sugar, boils for only two minutes, the reduction tables are constructed for an ebullition of four minutes, which yields higher results. Moreover, the hydrochloric acid used attacks constituents of the wort other than cane sugar, and augments their reducing power.

M. J. S.

**Estimation of Starch in Compressed Yeast.** By F. FILSINGER (*Chem. Zeit.*, 1894, 18, 742).—Twenty to thirty grams of the sample is rubbed with 250 c.c. of water, and mixed with excess of a solution of iodine in potassium iodide; the starch combines with the iodine, and forms a comparatively heavy compound, which settles long before any appreciable quantity of yeast has gone down. The milky liquid is syphoned off, and the iodide of starch repeatedly lixiviated

with water until all the yeast cells have been removed. The starch is finally collected on a weighed filter, dried at  $105^{\circ}$ , and weighed. The iodine is practically expelled during the heating. In calculating the percentage, it must be remembered that commercial potato starch generally contains 15 per cent. of water.

The test analyses are very satisfactory. When, however, the amount of starch is below 10 per cent., the results will be somewhat too low.

L. DE K.

**Estimation of Carbohydrates.** By E. SCHULZE (*Chem. Zeit.*, 1894, **18**, 527—528).—The author points out that if carbohydrates, on boiling with dilute sulphuric acid, yield other products besides dextrose, the action of the acid should not be unduly prolonged. If a mixture of carbohydrates be inverted, it is almost impossible to get a good result, as some of them may already have become largely decomposed before the inversion of the others is anything like complete.

L. DE K.

**Separation of Uric acid, Adenine, and Hypoxanthine.** By M. KRÜGER (*Zeit. physiol. Chem.*, 1894, **20**, 170—175).—In a hot solution containing the three substances, copper sulphate and sodium thiosulphate precipitate only adenine and hypoxanthine. In a cold solution of these two substances, the same reagents precipitate adenine only.

W. D. H.

**Estimation of Xanthine-like Substances in Urine.** By M. KRÜGER and C. WULFF (*Zeit. physiol. Chem.*, 1894, **20**, 176—185).—The new name alloxuric substances is suggested for those of the uric acid group. The alloxuric bases which occur in small quantities in urine are xanthine, guanine, hypoxanthine, carnine, paraxanthine, and heteroxanthine; a specific reagent for their precipitation is a mixture of copper sulphate with sodium hydrogen sulphite, but it also precipitates uric acid. 100 c.c. of urine is precipitated with 10 c.c. of these reagents, and the precipitate allowed to collect for two hours. Uric acid is separately determined in another sample of urine. The absolute amount of the nitrogen in this precipitate varies from 2.6 to 8 milligrams per 100 c.c. of urine, the average being 4.53.

The proportion of uric acid nitrogen to the nitrogen of the alloxuric bases varies from 2.1 : 1 to 7.6 : 1. The mean of 19 analyses gives 3.82 : 1. The average uric acid nitrogen in the 24 hours is 0.2333 gram; and of nitrogen in alloxuric bases, 0.0481 gram.

W. D. H.

**Estimation of Acidity in Milk.** By M. SCHAFFER (*Staz. Sper. Agrar.*, 1894, **26**, 164—167; from *Bern. Blätter f. Landw.*).—The apparatus used in the method described, which is a modification of the Soxhlet-Henkel method, consists of two cylindrical bulbs connected by a narrow graduated tube. The lower bulb holds just 50 c.c., and is provided at its lower end with a small bulb, holding 2 c.c. The upper of the two large bulbs is of about the same size as the lower, and is stoppered. In making a determination, 2 c.c. of phenolphthalein solution is poured into the apparatus (filling the

lowest portion of the apparatus), then the milk to be examined, until it reaches the 50 c.c. mark, and lastly,  $\frac{1}{4}$  normal soda solution (2—2.5 c.c.). The apparatus is then corked, and the contents mixed. More soda is gradually added until alkalinity is produced. The amount of alkali added is read off in the narrow tube. In mixing the alkali, the apparatus must not be shaken (as froth would be produced), but so inclined that the liquid runs into the upper bulb.

The method is of use in ascertaining whether milk is sufficiently free from acid to keep. It will probably also be of use in testing milk intended for cheese-making, and will furnish evidence of milk having been more or less skimmed (since milk always becomes more acid when left at rest), and the presence of such milk as an adulterant.

N. H. J. M.

**Soxhlet's Areometric Estimation of Fat in Milk.** By H. TIMPE (*Chem. Zeit.*, 1894, 18, 392—394).—This deservedly popular process has one great inconvenience, namely, that the ether sometimes refuses to properly separate from the alkaline solution, so that only a small amount can be drawn off.

The author now recommends that the sample of milk should first be diluted with three volumes of water. The ethereal layer then separates with the greatest ease.

L. DE K.

**Loss of Total Solids in Milk on Keeping.** By E. J. BEVAN (*Analyst*, 19, 241—244).—The author accidentally noticed that milk placed in the usual weighing dishes will, if not soon evaporated, yield a residue which may be as much as 1 per cent. too low. If immediately before evaporation the milk is carefully neutralised with N/10 soda, the loss will not be so great, owing to the formation of a stable lactate. Contrary to Bell's statement, the author finds lactic acid to be sensibly volatile in the presence of water. The results of several experiments are tabulated, and show the disproportion between the acidity and the loss in total solids.

L. DE K.

**Periodic Estimation of Volatile Fatty Acids in the Butter produced during a Year.** By L. CANTONI and L. CARCANO (*Staz. Sper. Agrar.*, 1894, 26, 131—137).—With the view of ascertaining the causes of the variations in the amount of volatile fatty acids in butter, samples of butter from three dairies were examined weekly for a year. The results, which are given in tables, do not show any great differences or regularity. This is, perhaps, due to the fact that in the Lombardy dairies calving does not take place at definite periods, and a kind of compensation may thus take place between conditions which raise and lower respectively the amount of volatile fatty acids.

A table is also given showing the results of experiments with Zeiss' butter-refractometer as well as the volatile fatty acids.

N. H. J. M.

**Modification of the Reichert-Meissl Butter Process.** By C. BÜNTE (*Chem. Zeit.*, 1894, 18, 204—206).—The author criticises the sulphuric acid process lately proposed by Kreiss and modified by

others, and has finally adopted the following plan. 5 grams of butter-fat is introduced into an Erlenmeyer litre flask, and heated for a time in a drying oven at  $100^{\circ}$ ; 10 c.c. of sulphuric acid (sp. gr. 1.8355) is added, and the mixture well agitated until all the fat has dissolved. The flask is now put into water at  $30-32^{\circ}$  for 10 minutes; 150 c.c. of water is added, and then strong solution of potassium permanganate until the liquid acquires a transitory pink colour. The liquid is then subjected to the usual distillation and titration.

L. DE K.

**Estimation of Lecithin in Plants.** By E. SCHULZE (*Zeit. physiol. Chem.*, 1894, **20**, 225—232, 252).—A critical reply to v. Bitto in reference to his method (*Abstr.*, 1894, ii, 402). W. D. H.

**Analysis of India-rubber Wares.** By R. HENRIQUES (*Chem. Zeit.*, 1894, **18**, 411—412, 441—444; compare *Abstr.*, 1892, ii, 399).—The author gives further instructions for the analysis of rubber wares. Adulteration with fatty matter or fatty surrogate (*faktis*) may be detected by treating a weighed quantity of the sample with alcoholic soda, as previously described, and noticing the loss in weight. If the sample contains much added mineral matter, it is best to first treat it with moderately strong acid before boiling with the alkali; as the latter dissolves small quantities of rubber, a correction must be made by deducting from the weight of the surrogate a quantity corresponding with 2.5 per cent. of the rubber actually found; soluble sulphur is, of course, allowed for. Asphalt, whether true bitumen or the artificial product, is another adulterant. In the absence of surrogate, 1 gram of the finely-divided sample is soaked for an hour in 30 c.c. of nitrobenzene. The insoluble mass is thrown upon a filter, gently pressed with a small pestle, and further washed with another 30 c.c. of the solvent; the mass is then transferred by means of a wash-bottle to a porcelain dish and boiled with water until all odour of nitrobenzene has disappeared; it is then dried and weighed. As rubber is not altogether insoluble in nitrobenzene, a correction must be made by deducting 2.5 per cent. from the asphalt for true rubber dissolved; soluble sulphur must also be allowed for. If the sample contains also oil surrogate, this must be first removed by treatment with alkali, in which asphalt is practically insoluble. The process becomes still more complicated if, besides asphalt, lamp-black is also present; this withstands the action of all ordinary solvents, and remains in consequence with the rubber. The author has found that in pure rubber there is a fairly constant atomic relation between the hydrogen and the carbon, which may be taken as 16:10. The residue containing the rubber + the lamp-black is therefore submitted to an organic combustion, and any excess of carbon put down to lamp-black.

The test analyses given by the author are remarkably satisfactory considering the nature of the analysis. The process does not, as yet, provide for a host of other possible adulterants. L. DE K.

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## General and Physical Chemistry.

**Indices of Refraction of Solutions of Sulphur and Phosphorus in Carbon Disulphide.** By V. BERGHOF (Zeit. physikal. Chem., 1894, 15, 422—436).—The indices of refraction of solutions of sulphur in carbon bisulphide for sodium light were determined at two different temperatures, 3·5° and 22·7°. The results are contained in the following table, the first column of which gives the concentrations of the solutions as the number of parts by weight of sulphur contained in 100 parts of carbon bisulphide.

	$n_{3.5}$	$n_{22.7}$	Diff. for 1°.	$n_{15}$ cal.
0	1·64143	1·62522	8443	1·63172
5	1·65153	1·63668	7735	1·64264
10	1·66175	1·64704	7662	1·65294
15	1·67170	1·65772	7281	1·66333
20	1·68105	1·66643	7647	1·67232
25	1·69073	1·67564	7860	1·68169

Solutions of phosphorus in carbon bisulphide were examined only at 20·7°. The numbers obtained were as follows.

Conc.	$n_{20.7}$
0	1·62697
5	1·64012
10	1·65216
15	1·66517
20	1·67628
25	1·68646

The sulphur solutions give constant values for the expression  $(n - 1)/d$ , but not for  $(n^2 - 1)/d(n^2 + 2)$ . Temperature appears to have little or no influence on the values of  $(n - 1)/d$ . H. C.

**Saturated Hydrocarbons containing the Active Amyl Radicle.** By Miss I. WELT (Compt. rend., 119, 743—747).—Ethylamyl, propylamyl, isobutylamyl, and diamyl were prepared by the action of sodium on mixtures of the appropriate alkylic iodides. When necessary, corrections were made for the small quantities of alkylic iodides present in the hydrocarbon. The rotatory powers are as follows.

	Low temperature.		High temperature.	
	$t$ .	$[\alpha]_D$ .	$t$ .	$[\alpha]_D$ .
Ethylamyl. . . .	17°	+ 6·23 to + 6·43	60°	+ 6·09
Propylamyl . .	16	+ 6·44	54	+ 6·25
Isobutylamyl ..	20	+ 5·88	51	+ 5·66
Diamyl . . . . .	17	+ 11·95	—	—
Diamyl . . . . .	21	+ 12·08	78	+ 12·06

All the hydrocarbons are dextrogyrate, and the rotatory power is only slightly affected by the temperature, although it tends to diminish. In the case of the hydrocarbons containing one asymmetric carbon, the rotatory power passes through a maximum, the exact position of which is not yet determined, although the calculated maximum corresponds with pentylamyl. The rotatory power of diamyl is nearly double that of the hydrocarbons containing only one amyl group, which is in agreement with the views of Guye and Gautier.

C. H. B.

**Attempts to Resolve Unsaturated Compounds into Optically Active Constituents.** By A. LE BEL (*Bull. Soc. Chim.*, 1894, [3], 11, 292—295).—The fact that the naturally occurring ethylene derivatives are optically inactive has tended hitherto to divert inquiry from the possibility of their activity. It is quite feasible, however, that by substituting sufficiently heavy groups for two of the hydrogen atoms in the ethylene molecule the latter might be caused to suffer sufficient deformation to give rise to such activity. A somewhat analogous case occurs in the series of diamine platinochlorides, the crystalline forms of which undergo modification as the molecular weight increases, this modification being probably due to internal stereometric rearrangement of the molecules.

The results of experiment, however, fail to confirm any such supposition. Both allylic alcohol and ammonium  $\alpha$ -crotonate (from  $\beta$ -hydroxybutyric acid) fail to show any signs of differentiation into optically active modifications when used as culture-media for moulds. Maleic and fumaric acids also yield practically inactive products. Mesoconic and citraconic acids at first seemed to give decisive evidence in favour of the theory, as the former yielded a dextrogyrate, the latter a lævogyrate, product when subjected to the above-mentioned process. In one experiment, 400 grams of citraconic acid in weak aqueous solution (0.2 per cent.) yielded a product, the methylic salt of which proved to be distinctly lævogyrate. As, however, the activity was found to reside in the least volatile portion, it was probably due to an impurity, and on repeating the experiment with slight modifications on a larger quantity (1400 grams), the impurity was isolated as a liquid which boiled at about 140°, and gave rise to a rotation of  $-10^\circ$  per 10 cm. It proved on analysis to be *methylic methylmalate*,  $\text{COOMe} \cdot \text{CHMe} \cdot \text{CH}(\text{OH}) \cdot \text{COOMe}$ , formed by hydration of the citraconate. The more volatile portion was also active, but proved on analysis to consist of a mixture of the citraconate and methylmalate. The results of the experiments with mesaconic and citraconic acids must, therefore, also be taken as negative, and the molecules of the simpler of the ethylene derivatives, at all events, must continue to be represented by plane formulæ.

JN. W.

**Rotatory Powers of Disubstituted Alkyl Tartrates.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1894, [3], 11, 305—317).—See this vol., i, 173.

**Determination of the Molecular Weight of Liquids.** By P. A. GUYE (*Compt. rend.*, 1894, **119**, 852—854).—The ratio of the molecular refraction to the critical coefficient (absolute critical temperature divided by the critical pressure) should theoretically be about 1·8. On the other hand, the quantity  $f$  given by the equation

$$f = \frac{(\log p_c - \log p)}{T_c - T} T,$$

where  $p_c$  and  $T_c$  are the critical pressure and absolute critical temperature, and  $p$  and  $T$  any other pressure and corresponding temperature, should have the value 2·8 to 3·1 if the molecule in the liquid state is of the same weight as the molecule at the critical point, or the value 3·2 to 4·1 if polymerisation has taken place. The author has calculated the values of the above two quantities for a number of liquid hydrocarbons, and comes to the conclusion that these have the same molecular weight in the liquid as in the gaseous state.

H. C.

**Scientific Electro-chemistry of the Present, and Technical Electro-chemistry of the Future.** By W. OSTWALD (*Zeit. physikal. Chem.*, 1894, **15**, 409—421).—A popular address to the German Electro-technical Association. The author deals with the modern theories of electro-chemistry, and points to technical improvements for the future, more particularly in the construction of secondary batteries, and the direct conversion of the energy of burning coal into electricity.

H. C.

**Thermoelectric Properties of Pure Metals.** By K. NOLL (*Ann. Phys. Chem.*, 1894, [2], **53**, 874—911).—Owing to considerable differences between the observations of different workers on the thermoelectric properties of metals, the author redetermines the electromotive force for various combinations, employing metals in as high a state of purity as was obtainable. In the first series of experiments, the second metal was in all cases mercury, and the temperatures of the junctions 100° and 0°. The E.M.F. was determined by Du Bois Raymond's modification of Poggendorf's methods, Clarke cells being employed as the source of the constant E.M.F. The results of these researches (expressed in microvolts) are contained in the following table, + values indicating a current from mercury to metal at the hot junction.

Bismuth.....	−6705·4	Carbon rod.....	+ 662·88
Nickel .....	−1664·2	Silver .....	+ 710·25
Cobalt .....	−1522·2	Gold .....	+ 713·35
Nickel silver...	−1085·2	Copper .....	+ 725·58
Platinum.....	+ 4·59	Zinc .....	+ 692·71
Aluminium....	+ 362·4	Cadmium .....	+ 875·09
Magnesium....	+ 391·84	Carbon filament .	+ 1452
Tin.....	+ 396·03	Iron.....	+ 1601·4
Lead .....	+ 402·5	Piano wire .....	+ 1732·3
Brass.....	+ 443·31	Antimony.....	+ 3379·6

In many cases the effect of small quantities of impurity was very great. Thus platinum gave values as high as +593·88, and copper



as low as +684.29 when the metals were not chemically pure. The state of aggregation had also a marked effect in some cases, for instance, silver (710.25; 671.51), zinc (692.71; 735.2), iron, brass, nickel. The second series of experiments was performed at various temperatures between 217° and 0°, a number of experiments being made in each case. From the results, the value for 100—0° was calculated, good agreement with the observed value being in all cases obtained. The junctions were in some cases formed with mercury, in others with copper. The electromotive force is given according to Gangain by formula  $\epsilon = (t_1 - t_2)\{b \pm c(t_1 + t_2)\}$ . The values for  $b$  and  $c$  are deduced from two experiments, and the results calculated by their aid compared with the observations. The agreement is perfectly satisfactory. The value  $\frac{d\epsilon}{dt} = b \pm ct$  is then calculated, and as this can be expressed as  $b \pm (k_2 - k_1)t$ , where  $k_2$  and  $k_1$  are the constants for the different metals of the junction, the numbers are referred to lead for which  $k = 0$ . The values thus obtained for the thermoelectric power  $\frac{d\epsilon}{dt}$  are compared with those of other observers. The difference in the result may be explained by the effect of impurities which, as is evident from the numbers, produce considerable variations.

L. M. J.

### Conductivity of Aqueous Solutions of Carbonic Anhydride.

By W. F. KNOX (*Ann. Phys. Chem.*, 1894, [2], 54, 44—57).—Kohlrausch's method was employed for the determination of the conductivity, and a number of experiments at varying pressures were made, the results being recorded for both rising and falling pressures. As the temperature was not constant, varying to the extent of about a degree, the results were reduced to constant temperature by use of the formula  $\frac{dk}{dt} = \frac{\partial k}{\partial t} + \frac{\partial k}{\partial Q} \cdot \frac{\partial Q}{\partial t}$ , where  $Q$  is the quantity of carbonic anhydride dissolved. This reduced to  $\frac{dk}{k} = \frac{1}{k} \frac{\partial k}{\partial t} \cdot dt + \frac{1}{2Q} \cdot \frac{\partial Q}{\partial t} \cdot dt$ . The value for the latter term is found to be -0.0169 at 12.5 and -0.0099 at 18°, and for the former 0.0300 and 0.0257 for the same temperatures, which are those to which the results are reduced. Tables are then given of the reduced numbers, corrections being also made for the conductivity of pure water. If  $m$  is the equivalent ( $\frac{1}{2}\text{CO}_2$ ) content per litre, then  $k/\sqrt{m}$  should be approximately constant. The value for this expression is determined, a variation of from 121 to 139 being observed at 12.5°, and of from 144 to 159 at 18°; the value for  $m$ , however, varying between 0.002 and 0.2. If also the value for the most dilute solution is neglected, the numbers at 18° only vary between 147 and 144. The time taken to saturate water by passing a stream of carbonic anhydride through it was also observed, together with the time required to free it from the gas by a current of air. In the latter case the curve of decrease of saturation is approximately logarithmic. The author points out that the increase in conductivity of pure water

when exposed to the air is probably due to the solution of carbonic anhydride (compare Abstr., 1894, ii, 375). L. M. J.

**Heat of Vaporisation of Saturated Fatty Alcohols.** By W. LOUGUININE (*Compt. rend.*, 1894, **119**, 601—604).—The alcohols were carefully purified, and precautions were taken to exclude moisture at every stage of the operations. The method adopted was similar to that of Regnault, but only 100 c.c. of liquid was employed. The differences between the author's results and those of previous observers, is probably due to the care taken to exclude moisture. In the case of isopropyl alcohol and isobutyl alcohol, it was assumed that the specific heat of the liquid is the same as for the corresponding normal alcohol, and that the specific heat of dimethylethylcarbinol is the same as that of fermentation amylic alcohol. The results are as follows, the determinations being made under a pressure of 745—755 mm.

Ethyl alcohol .....	201.42	cal.
Normal propyl alcohol .....	164.07	"
Isopropyl alcohol .....	159.72	"
Normal butyl alcohol .....	138.18	"
Isobutyl alcohol .....	136.16	"
Amylic alcohol (fermentation) ..	118.15	"
Dimethylethylcarbinol .....	110.37	"

C. H. B.

**Trouton's Law and the Saturated Fatty Alcohols.** By W. LOUGUININE (*Compt. rend.*, 1894, **119**, 645—647).—Trouton's law, that the product of the molecular weights of substances into their latent heats of vaporisation, divided by their boiling points in absolute temperature, is a constant quantity, holds good for the saturated alcohols of the fatty series (compare preceding Abstract).

	M.	<i>t.</i>	<i>r.</i>	$\frac{Mr}{T + t}$
Ethyl alcohol .....	46	78.3°	201.42	26.37
Propyl alcohol .....	60	96.96	164.07	26.61
Isopropyl alcohol .....	60	82.19	159.72	26.98
Butyl alcohol .....	74	116.48	138.18	26.25
Isobutyl alcohol .....	74	107.67	136.16	26.47
Amylic alcohol (fermentation) ..	88	130.06	118.15	25.79
Dimethylethylcarbinol .....	88	102.08	110.37	25.90

The boiling points correspond with a pressure of about 750 mm. and the mean value of the constant is 26.34. Schiff's results with ethereal salts of the acetic series give about 21, and for the hydrocarbons of the benzene series about 20. The results of Berthelot and Ogièr with formic and acetic acids give different values, but in these cases the vapour is not normal. If, however, the values for normal vapour are taken, the constant becomes 25.9 for acetic acid. It follows that the

value of the constant  $\frac{Mr}{T + t}$  remains practically constant for a given series of compounds, although it varies from one series to another. Trouton's empirical law is therefore capable of wide and important

application, and makes it possible to calculate the latent heats of vaporisation of a whole series of compounds, if the value for one of them is known.

C. H. B.

**Heat of Combustion of Glycogen.** By F. STOHMANN and R. SCHMIDT (*J. pr. Chem.*, 1894, [2], 50, 385—387).—The glycogen employed was extracted from the liver of a rabbit by means of water, no alkali being used. After purification by precipitation with alcohol in the presence of hydrochloric acid and potassium mercury iodide, it was dried, extracted with ether to remove a small amount of fat, and then again dried at 120°. Ignition was ensured by the addition of a small piece of collodion. The following table shows the results obtained, compared with the corresponding data for cellulose and starch.

	Heat of combustion.	
	Per gm. cal.	Per gm. mol. Cal.
Glycogen.....	4190·6	678·9
Cellulose.....	4185·4	678·0
Starch.....	4182·5	677·5

The heat of formation of glycogen is therefore 230·1 Cal.

A. H.

**Thermochemistry of the Isomeric Acids of the Composition  $C_7H_6O_3$  and  $C_8H_8O_3$ .** By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.*, 1894, [2], 50, 388—400).—The following table contains the heats of combustion and formation of a number of these acids, compared with their electrical conductivity, as determined by Ostwald and others.

	Heat of combustion. Cal.	Heat of formation. Cal.	Electrical conductivity. <i>k</i> .
Hydroxybenzoic acid [ortho] ...	727·1	137·9	0·102
"    "    [meta]....	726·6	138·4	0·0087
"    "    [para]....	725·9	139·1	0·00286
Hydroxytoluic acid			
[COOH : Me : OH = 1 : 2 : 6]..	883·4	144·6	0·106
"    "    [1 : 3 : 2]..	879·3	148·7	0·1018
"    "    [1 : 5 : 2]..	880·1	147·9	0·00841
"    "    [1 : 4 : 2]..	878·4	149·9	0·0684
Anisic acid [OMe : COOH = 1 : 4]	895·2	132·8	0·0032
Mandelic acid.....	890·9	137·1	0·0417
Phenoxyacetic acid.....	903·3	124·7	0·0756
Orthohydroxymethylbenzoic acid			
[COOH : CH <sub>2</sub> : OH = 1 : 2]....	887·8	142·2	0·015
Phthalide.....	884·7	74·3	—

It appears that both heat of combustion and electrical conductivity are greatest for the ortho-acids and least for the para-acids.

Taking the heat of combustion of benzoic acid as 771·7, and of the toluic acids as 929·4 (ortho), 929·1 (meta), and 927·4 (para), it follows that the substitution of hydroxyl for hydrogen in benzoic acid

diminishes the heat of combustion by 44·6 (ortho), 45·1 (meta), and 45·8 (para) Cal., whilst in the toluic acid series the numbers vary from 46—49·8 Cal.

The substitution of methyl for hydrogen, on the other hand, increases the heat of formation by the following amounts.

Benzoic acid, ortho .....	157·7 Cal.
„ meta .....	157·4 „
„ para .....	155·7 „
Salicylic acid, Me = 6 .....	156·3 „
„ Me = 3 .....	152·2 „
„ Me = 5 .....	153·0 „
„ Me = 4 .....	151·3 „

The substitution of methyl for hydrogen, however, gives rise to different results, according as this hydrogen atom is combined with carbon, nitrogen, or oxygen. The same relations hold with the group  $\text{CH}_2\text{COOH}$ , so that it may be concluded that a carbon atom which combines with a nitrogen atom requires an amount of energy equal to 10—12 Cal., and one which combines with an oxygen atom 15—20 Cal. more than one which combines with another carbon atom. The actual values obtained were

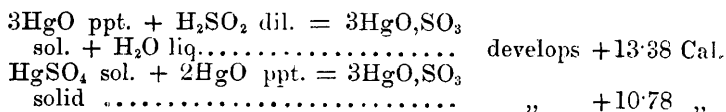
	$\text{CH}_3$ .	$\text{CH}_2\text{COOH}$ .
With C .....	156·6 Cal.	150·9 Cal.
„ N .....	166·6 „	162·7 „
„ O .....	171·7 „	170·8 „

By means of these numbers, the heats of formation of the various acids can be approximately calculated from those of the simpler acids from which they are derived by substitution. A. H.

**Mercuric Sulphates.** By R. VARET (*Compt. rend.*, 1894, 119, 684—687).—The heat of dissolution of mercuric sulphate in dilute sulphuric acid is +4·35 Cal. at 16·5°, and +4·90 Cal. at 14°. Measurement of the heat developed by the action of hydrochloric acid on mercuric sulphate, sulphuric acid on mercuric chloride, hydrocyanic acid on mercuric sulphate and sulphuric acid on mercuric cyanide, sulphuric acid and sodium chloride on mercuric sulphate, and other similar reactions give, as a mean value

HgO ppt. + $\text{H}_2\text{SO}_4$ dil. = $\text{HgSO}_4$ diss. + $\text{H}_2\text{O}$ liq. ....	develops + 2·6 Cal.
HgO ppt. + $\text{H}_2\text{SO}_4$ liq. anhyd. = $\text{HgSO}_4$ sol. + $\text{H}_2\text{O}$ liq. ....	„ + 19·6 „
HgO ppt. + $\text{SO}_3$ solid = $\text{HgSO}_4$ solid..	„ + 40·1 „
Hg liq. + S solid + $\text{O}_4$ gas = $\text{HgSO}_4$ solid .....	„ + 166·1 „

The dissolution of basic mercuric sulphate in dilute sulphuric acid develops +9·1 Cal., and reactions similar to those employed in the case of the normal sulphate give the following result.



The action of a large quantity of water on normal mercuric sulphate does not result in its complete conversion into the basic sulphate, owing to the simultaneous formation of an acid sulphate, with development of heat. The maximum thermal disturbance corresponds with the formation of a solution containing sulphuric acid, and saturated with the basic sulphate. Sulphuric acid is completely displaced from mercuric sulphate by even very dilute hydrocyanic acid, and is also displaced almost, if not quite, completely by hydrochloric acid.

C. H. B.

**Relation between the Vapour Pressures of a Substance in the Solid and Liquid State.** By A. PONSOT (*Compt. rend.*, 1894, 119, 791—794).—The author has formerly shown that for ice and water

$$RT \log \frac{F}{f} = E \left[ \frac{l_0}{T_0} (T_0 - T) - (C_c - C_g) T \left( \frac{T_0 - T}{T} - \log \frac{T_0}{T} \right) \right].$$

$F$  and  $f$  being the vapour tensions at  $T$ ,  $l_0$  the latent heat of fusion at  $T_0$ , the temperature of the triple point,  $C_c$  and  $C_g$  the specific heats of water and of ice. This relationship is now shown to hold good in the cases of benzene and acetic acid.

H. C.

**The Absorption Coefficients of Carbonic Anhydride and Hydrogen Sulphide in Water at the Freezing Point.** By K. PRYTZ and H. HOLST (*Ann. Phys. Chem.*, 1894, [2], 54, 130—138).—If a current of gas be passed through pounded ice, the temperature sinks to that of the freezing point of a saturated aqueous solution of the gas, which may be calculated by the usual formulæ. For carbonic anhydride and hydrogen sulphide, the authors find the depressions to be respectively  $0\cdot156^\circ$  and  $0\cdot392^\circ$ , the calculated numbers being  $0\cdot158$  and  $0\cdot377$ . The absorption coefficients were then determined, both at zero and at the freezing point of the solution. The method consisted in passing a stream of the gas through (or addition of solid carbonic anhydride to) the water contained in a flask; finding the quantity of gas contained by weighings, and correcting for that above the liquid by measurement of manometric pressure. Corrections are made for small quantities of foreign gases unavoidably present. For carbonic anhydride at  $0^\circ$ , they obtained the value  $1\cdot7308$ , and at  $-0\cdot15^\circ$   $1\cdot7375$ , whilst hydrogen sulphide gave the value  $\alpha_0 = 4\cdot6796$ . Bunsen found a value  $\alpha_0 = 1\cdot7967$  for the former gas, but this was obtained by extrapolation, the lowest observed temperature being  $4\cdot4^\circ$ . Henrich obtained the value  $1\cdot7326$  (*Abstr.*, 1892, 1044). The value  $4\cdot6796$  also is considerably higher than that found by Schönfeld and Carius for the same gas; this the authors consider is due to the fact that these observers did not use completely saturated solutions.

L. M. J.

**New Reaction Illustrating the Phenomenon of Dissociation.**

By A. GUNN (*Chem. News*, 1894, **70**, 223—224).—When ammonia (sp. gr. 0·880) is added, drop by drop, to a solution containing 0·2 gram of zinc sulphate in 5 c.c. of water, until it is 1 or 2 drops in excess of the quantity required to re-dissolve the precipitate, and 10 or 12 drops of a 10 per cent. solution of sodium phosphate and 5 c.c. of water are also added, a perfectly bright solution is obtained, which on heating acquires a turbidity that increases to a thick curdy precipitate in the boiling liquid; the mixture, however, regains its original brightness and freedom from any precipitate on cooling. The operation may be repeated many times if loss of ammonia is avoided. When the excess of ammonia is removed by drawing air through the cold solution, a precipitate is obtained which contains ammonia; whereas the precipitate obtained from the boiling solution does not contain ammonia; hence the formation of the precipitate in the latter case appears to be due to dissociation.

D. A. L.

**Experimental Proof of the Laws of Van't Hoff, Arrhenius, and Ostwald for Dilute Solutions.**

By M. WILDERMANN (*Zeit. physikal. Chem.*, 1894, **15**, 337—357).—The freezing points of very dilute solutions have been determined with great care and every precaution to secure the highest attainable degree of accuracy. Experiments with the non-electrolytes cane-sugar, carbamide and alcohol show that these in the most dilute solutions give results in perfect accordance with van't Hoff's well known formula for the molecular reduction  $0\cdot02 T^2/w$ , if for  $w$  the value 80 Cal. is taken. The electrolytes, sulphuric acid, potassium chloride, di- and tri-chloroacetic acid, and orthonitrobenzoic acid all give reductions of the freezing point of water which are in accordance with the view that these substances have undergone electrolytic dissociation to the degree indicated by the conductivity measurements of the corresponding solutions. The dissociation calculated from the freezing points is, however, somewhat smaller than that calculated from the conductivities, which may in part be accounted for by the presence of higher non-dissociated and dissociated molecules in the solution (comp. Abstr., 1893, ii, 509). The accuracy attained in these experiments is sufficient to enable calculations to be made of the affinity coefficients from Ostwald's law of dilution in the cases of dichloroacetic acid and orthonitrobenzoic acid. The calculated value is practically independent of the dilution in each case, but is somewhat smaller than that obtained from the conductivity.

H. C.

**Determination of the Freezing Point of Water.**

By M. WILDERMANN (*Zeit. physikal. Chem.*, 1894, **15**, 358—364).—In determining the freezing point of water or of very dilute aqueous solutions, an error is introduced, owing to the fact that from such solutions the ice separates out in fine crystals which cake round the bulb of the thermometer, this occurring before the thermometer indicates the temperature of the solution. The layer of ice being a bad conductor, an error is introduced of  $0\cdot0015$ — $0\cdot0017^\circ$  in the temperature registered as the freezing point. To obviate this, the author allows the solution

under examination to partially solidify before the thermometer, which has been previously cooled below the melting point to be observed, is introduced. The ice does not crystallise out round the bulb under these circumstances, and the mercury rises to the true melting point.

H. C.

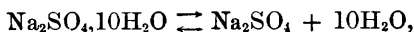
**Freezing of Sulphuric acid Solutions.** By R. PICTET (*Compt. rend.*, 1894, **119**, 642—645).—Four series of experiments were made with mixtures containing increasing proportions of either water or sulphuric acid. The results of all the series were found to agree, provided that congelation was allowed to take place very slowly and the temperature of the cold chamber was kept as high as was consistent with the freezing of the liquid; if these precautions are not observed, the results are not concordant. The curve of the temperatures of crystallisation cuts the zero line five times, but the points of maxima and minima do not correspond with definite hydrates except in the case of the decahydrate  $\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , which freezes at  $-88^\circ$ . The liquid contains more sulphuric acid than the crystals when the freezing point falls on a descending part of the curve, but the reverse is the case when it falls on an ascending part of the curve. Whilst at the points of maxima and minima the liquid and the crystals have the same composition. The results are given in the following table.

Formula.	Percentage of sulphuric acid.	Sp. gr.	Freezing point.
$\text{H}_2\text{SO}_4$ .....	100.00	1.842	+10.5°
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ .....	84.48	1.777	+ 3.5
$\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ....	73.08	1.650	—70
$\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$ ....	57.65	1.476	—40
$\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$ ....	47.57	1.376	—50
$\text{H}_2\text{SO}_4 + 8\text{H}_2\text{O}$ ....	40.50	1.311	—65
$\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O}$ ...	35.25	1.268	—88
$\text{H}_2\text{SO}_4 + 11\text{H}_2\text{O}$ ...	33.11	1.249	—75
$\text{H}_2\text{SO}_4 + 12\text{H}_2\text{O}$ ...	31.21	1.233	—55
$\text{H}_2\text{SO}_4 + 13\text{H}_2\text{O}$ ...	29.52	1.219	—45
$\text{H}_2\text{SO}_4 + 14\text{H}_2\text{O}$ ...	28.00	1.207	—40
$\text{H}_2\text{SO}_4 + 15\text{H}_2\text{O}$ ...	26.63	1.196	—34
$\text{H}_2\text{SO}_4 + 16\text{H}_2\text{O}$ ...	25.39	1.187	—26.5
$\text{H}_2\text{SO}_4 + 18\text{H}_2\text{O}$ ...	23.22	1.170	—19
$\text{H}_2\text{SO}_4 + 20\text{H}_2\text{O}$ ...	21.40	1.157	—17
$\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$ ...	17.88	1.129	— 8.5
$\text{H}_2\text{SO}_4 + 50\text{H}_2\text{O}$ ...	9.82	1.067	— 3.5
$\text{H}_2\text{SO}_4 + 75\text{H}_2\text{O}$ ...	6.77	1.045	0.00
$\text{H}_2\text{SO}_4 + 100\text{H}_2\text{O}$ ..	5.16	1.032	+ 2.5
$\text{H}_2\text{SO}_4 + 300\text{H}_2\text{O}$ ..	1.78	1.007	+ 4.5
$\text{H}_2\text{SO}_4 + 1000\text{H}_2\text{O}$ .	0.54	1.001	+ 0.5

C. H. B.

**Pressure of Solution as a Means of Determining the Temperature of Change.** By J. VERSCHAFFELT (*Zeit. physikal. Chem.*, 1894, **15**, 437—456).—From the analogy between the process of vaporisation and that of solution, Nernst concludes that substances have a certain solution pressure analogous to their vapour pressure.

Since in many cases a change in the composition of a substance, as for example in a salt containing water of crystallisation, is indicated by an abrupt change in the vapour pressure, a change in composition should also be indicated by a change in the pressure of solution. This method is applied to an examination of the decomposition of crystallised sodium sulphate.



the behaviour of the salt towards mixtures of amyl alcohol and water at different temperatures being observed. The temperature of change is found to be  $32.74^\circ$ , corresponding with the temperature of maximum solubility.

From the results obtained, the value of Van't Hoff's coefficient  $i$  for water dissolved in amyl alcohol is calculated. This calculation points to a complex molecule of at least  $(\text{H}_2\text{O})_4$ . H. C.

**Correct Formulæ for Osmotic Pressure; Change of Solubility, Melting and Boiling Points; Heats of Solution and Dilution in Dissolved Dissociated Substances.** By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1894, **15**, 457—497).—Thermodynamical calculations not suitable for abstracting. H. C.

**Rate of Hydrolysis of some Ethereal Salts.** By R. LÖWENHERZ (*Zeit. physikal. Chem.*, 1894, **15**, 389—398).—A continuation of the work of De Hemptinne (Abstr., 1894, ii, 274), the chief result of whose investigations was that the nature of the alcohol was of little influence, that of the acid of great influence, on the rate of hydrolysis of ethereal salts. In order to study the influence of the alcohol, the acetates of glycerol and phenol were examined. The influence of the acid was studied by taking ethereal salts of formic, mono-, di- and tri-chloroacetic, and benzoic acids, and also ethylic iodide. The results fully confirm De Hemptinne's conclusions. The ratio of the constants of the velocity equation in the case of the greatest variation for the alcohols (methyl alcohol and phenol) is only about 2 to 1, but the greatest variation for the acids (formic and benzoic acids) is about 3700 to 1. H. C.

**Position of Magnesium in the Genetic System of the Elements; Atomic Volumes; Allotropes and Isomerides.** By C. T. BLANSHARD (*Chem. News*, 1894, **70**, 235, 271—272, 295—296).—It is pointed out that the atomic volume, the analysis of the spectrum, the volume heat (sp. ht.  $\times$  sp. gr.) suggest the classification of magnesium with calcium, strontium and barium instead of with zinc cadmium and mercury; but the atomic heat, on the other hand, places it between beryllium and zinc.

The author furnishes a table of atomic volumes based on the most recent or best authenticated values for atomic weights and specific gravities. Furthermore, he shows, from tabulated data relating to atomic volumes, specific heats, heats of combustion, boiling points and specific gravities, that the relationship which exists between these properties in the allotropic forms of elements is similar to what



it is in isomeric inorganic and organic compounds, which may indicate a similarity in constitution as regards elements and those compounds.

D. A. L.

**The Chemometer.** By W. OSTWALD (*Zeit. physikal. Chem.*, 1894, **15**, 399—408).—To any instrument that would be capable of measuring the chemical intensity of a system, or that would show whether any two systems were in chemical equilibrium, the name "chemometer" may be given. The author discusses generally the conditions which such an instrument would have to fulfil, and points out that for electrolytes the electrometer may be considered as a chemometer, as chemical intensity and E.M.F. are proportional to one another.

H. C.

**Preservation of Chemically Pure Alkaline Solutions.** By A. v. KALECSINSZKY (*Zeit. anorg. Chem.*, 1894, **7**, 384—385).—The author employs a glass bottle having a removable metallic bottom, and thin beakers of platinum or silver, of such a size that they just fit into the glass bottle. The alkaline solution comes into contact only with the metallic beaker. The flask is closed with a rubber cork and fitted with tubes as in the case of an ordinary wash bottle, the longer tube is, however, made of platinum or silver.

E. C. R.

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## Inorganic Chemistry.

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**Combination of Hydrogen Fluoride with Water.** By R. METZNER (*Compt. rend.*, 1894, **119**, 682—684).—Neither anhydrous hydrogen fluoride nor a mixture containing 30 per cent. of water solidifies at  $-70^{\circ}$ , but at about  $-45^{\circ}$  the "pure" acid of commerce, which contains about 43.4 per cent. of hydrogen fluoride, gradually deposits small, hard, opaline masses. If some of this solid mass is placed in acid containing 70 per cent. of the fluoride and cooled to  $-70^{\circ}$ , it sinks and rapidly dissolves. When an acid containing 55 per cent. is slowly cooled to about  $-45^{\circ}$ , it is converted into small, truncated prisms which have the composition  $\text{HF}, \text{H}_2\text{O}$ , and melt at  $-35^{\circ}$ , the temperature remaining constant until the change is complete. The crystals fume in the air, dissolve readily in the cold concentrated acid, and are heavier than it and than the commercial acid, which has a sp. gr. of 1.15. Since the sp. gr. of the anhydrous acid is 0.988, it follows that mixtures of the acid and water show a point of maximum contraction, which probably corresponds with the monhydrate. The monhydrate readily forms supersaturated solutions. There is no evidence of the existence of a hydrate  $\text{HF}, 2\text{H}_2\text{O}$ , although the acid that distils without change approximates to it in composition. This acid solidifies when strongly cooled, but the crystals have no definite melting point and seem to be a mixture of the monhydrate and ice.

C. H. B.

**Formation of Ozone by the Action of Electric Oscillations.**

By E. WIEDEMANN and G. C. SCHMIDT (*Ann. Phys. Chem.*, 1894, [2], **53**, 924—927).—The authors show that if, in the preparation of ozone by the influence of the silent discharge, means are adopted to obtain oscillations of a regular periodic nature, the yield of ozone is increased. They, however, only worked at low pressures where the yield of ozone was small, namely, 0.12 per cent., under the most favourable conditions.

L. M. J.

**Gases from Wood Charcoal at a High Temperature.**

By DOSMOND (*Compt. rend.*, 1894, **119**, 733—735).—When wood charcoal is heated to redness out of contact with air, it gives off from 170 to 250 litres of gas per kilo. The gas has the mean composition  $\text{CO}_2$ , 9.14; O, 0.26; CO, 18.08; H, 49.11;  $\text{CH}_4$ , 16.04; N, 7.37 = 100.00, and its antiseptic properties are superior to those of carbonic oxide. The greater part of the gas is probably formed by the pyrogenic decomposition of solid or liquid carbon compounds condensed in the charcoal. It would seem that in cases of poisoning by so-called charcoal fumes, the carbonic oxide is not simply a result of incomplete combustion.

C. H. B.

**Influence of certain Metals on the Stability of Ammonium Amalgam.**

By G. MICHAUD (*Amer. Chem. J.*, 1894, **16**, 488—490).—Having examined the behaviour of a saturated solution of ammonium chloride with mixtures of sodium amalgam and amalgams of silver, aluminium, gold, bismuth, cadmium, cobalt, copper, iron, magnesium, manganese, lead, platinum, antimony, tin, and zinc respectively, the author arrives at the following conclusions:—(i.) That when the radicle ammonium is set free in presence of an alloy of mercury with one of the aforesaid metals, its stability is inferior to what it would be when associated with mercury alone. (ii.) That a very small percentage of platinum absolutely prevents the formation of the ammonium amalgam. (iii.) That the power of decreasing the stability of the radicle ammonium is greater in the electro-negative metals, but is not proportional to their polarity. (iv.) That in spite of the contrary conclusion of several chemists (compare Landolt, *Zeit. f. Chem.*, 1869, **12**, 429), the amalgam of ammonium does contain ammonium, for whenever a simple mixture of hydrogen and ammonia is evolved during the experiment, it has not the power to dilate the mercury and to give it the characteristic appearance of the amalgam of ammonium.

G. T. M.

**Ammonium Orthophosphate.**

By K. KRAUT (*Zeit. anorg. Chem.*, 1894, **7**, 392).—In reference to Schottländer's remarks (this vol., ii, 64), the author points out that he had already shown in 1855 that the sparingly soluble crystals sometimes obtained on adding ammonium phosphate solution to ammoniacal liquids, have the composition  $\text{PO}_4(\text{NH}_4)_3 \cdot 3\text{H}_2\text{O}$ .

E. C. R.

**Presence of Ammonia in Zinc Powder.**

By F. ROBINEAU and G. ROLLIN (*Zeit. anal. Chem.*, **33**, 594; from *Moniteur scientifique*, [4], **7**, 138).—Zinc powder contains ammonia, partly in a form

soluble in hot water, partly also in combination, from which it is set free by boiling with soda. It can be entirely freed from ammonia by boiling and washing with dilute sulphuric acid (1—100), but, after drying in purified air, ammonia can again be detected in it.

M. J. S.

**Conversion of Black Mercury Sulphide into the Red Modification and the Density and Specific Heat of the two Modifications.** By W. SPRING (*Zeit. anorg. Chem.*, 1894, **7**, 371—383).—The ordinary black mercury sulphide cannot be converted into the red modification by pressure. Theoretically, it would require a pressure of 35,000 atmospheres. The author has obtained a new black modification of mercury sulphide by subliming ordinary mercury sulphide in the presence of a sufficient quantity of an inert gas. It is a micro-crystalline powder, is converted into the red modification by treatment with yellow ammonium sulphide, and has sp. gr. = 8.0395 at 17°. When subjected to a pressure of 100 atmospheres, it is easily converted into the red modification.

The red sulphide, when heated at 250—320°, turns black, but regains its red colour on cooling, whether it be cooled slowly or quickly. After being heated at 410°, it, however, remains black on cooling.

The sp. gr. of the ordinary black modification varies from 7.6242 at 18.3° to 7.5610 at 77.8°. The sp. gr. of the red modification, obtained by treating the black modification with ammonium sulphide, varies from 8.1289 at 21.6° to 8.0902 at 77.7°. The sp. gr. of the red modification, obtained by sublimation, varies from 8.1587 at 15.8° to 8.0978 at 77.7°. If the numbers obtained between these temperatures are represented graphically, parallel curves are obtained, showing that the volume for all the modifications varies in the same manner. Similar parallel curves are obtained by representing graphically the specific heats of the three modifications at different temperatures. The specific heat of the black sulphide varies from 0.0835 at 25—30° to 0.1433 at 75—80°; that of the red sulphide from 0.0749 at 25—30° to 0.1270 at 75—80°.

E. C. R.

**Temperatures of Transformation of Irons and Steels.** By G. CHARPY (*Compt. rend.*, 1894, **119**, 735—737).—The metals were heated in a small furnace, the source of heat being a platinum wire, through which an electric current was passed, and the temperatures were

	$a_1$		$a_2$		$a_3$	
	Heat- ing.	Cool- ing.	Heat- ing.	Cool- ing.	Heat- ing.	Cool- ing.
Steel containing						
Carbon 0.07 per cent. . .	—	—	740°	730°	865°	840°
"    0.09    "    ..	722°	664°	744	731	903	860
Carbon 0.07 per cent., nickel 1.15 per cent. .	710	698	744	732	835	—
Carbon 0.08 per cent., chromium 0.75 per cent.	—	675	744	744	860	789
Carbon 0.11 per cent., tungsten 0.60 per cent.	—	630	749	740	923	877

automatically recorded by a Le Chatelier pyrometer. The table on p. 110 gives the critical temperatures observed during heating and cooling, the critical points being distinguished by the letters  $a_1$ ,  $a_2$ ,  $a_3$  used by Osmond.

With these very soft steels, the point  $a_1$ , which is usually more marked the higher the proportion of carbon, is only feebly indicated, and the point  $a_3$  varies greatly both with the nature of the metal and the rate of heating. The point  $a_2$ , on the other hand, is very constant, and seems to indicate a distinctly reversible change, since it is produced at the same temperature during both heating and cooling. Arnold has also observed this constancy of the point  $a_2$  in soft steels.

Mechanical tests made after tempering indicate that the rectilinear break in the curve of extension disappears when the metal has been heated to  $750$ — $880^\circ$  and then tempered. When the same steels are heated, after having been drawn in the cold, the curves, as a rule, are identical with those given by the annealed metal, and this is true also of the tempered metals, which indicates that the changes produced by tempering or hardening are not permanent in the cold, and disappear on annealing at a temperature below the temperature of transformation. By rapid heating, however, curves were obtained in which the point  $740^\circ$  did not exist or was replaced by a convexity extending from  $720^\circ$  to  $740^\circ$ .

The facts observed show that the point  $a_1$  ( $690$ — $700^\circ$ ) corresponds with the transformation of the carbon estimated by Eggertz's method, a transformation which markedly increases the hardness of the steel; the point  $a_2$  ( $740^\circ$ ) corresponds with the transformation of iron which is characterised by the rectilinear break in the curve of extension, and which slightly modifies the magnetic and mechanical properties; the point  $a_3$  ( $860^\circ$ ) corresponds with a second transformation of the iron which seems to affect more particularly the magnetic properties.

C. H. B.

**Action of Ferric Acetate on Potassium Iodide and Hydrogen Iodide.** By K. SEUBERT and R. ROHRER (*Zeit. anorg. Chem.*, 1894, **7**, 393—405; see also this vol., ii, 17).—Ferric acetate and potassium iodide do not react with liberation of iodine, either in neutral solution or in the presence of a large excess of acetic acid. If, however, hydrochloric or sulphuric acid is added to the mixture, iodine is set free, and when the ratio of acid to the ferric acetate is 3 equivalents to 1 equivalent, the quantity of iodine liberated is equal to that liberated by an equivalent quantity of ferric chloride or sulphate.

Ferric acetate liberates iodine from hydrogen iodide, but when the proportions employed are 1 mol. hydrogen iodide and 1 equivalent of ferric acetate, the quantity of iodine liberated is considerably less than in the case of ferric chloride and ferric sulphate. When 10 mols. of hydrogen iodide are employed for 1 equivalent of ferric salt, 99 per cent. of the theoretical amount of iodine is liberated in all three cases. The addition of hydrochloric or sulphuric acid to the mixture  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3 : \text{HI}$ , increases the amount of iodine liberated until it nearly approaches the amount liberated in the case of ferric chloride and sulphate.

E. C. R.

**Methods of Removing the Phosphoric acid as Alkali Phosphate from Phosphates of Calcium and Iron.** By E. A. SCHNEIDER (*Zeit. anorg. Chem.*, 1894, **7**, 386—391).—The hydrogel obtained by dialysing a solution of ferric chloride saturated with normal calcium orthophosphate contains ferric oxide and phosphoric anhydride in the proportion 55.29 : 44.71 (Abstr., 1893, ii, 573). When the solution of this hydrogel in ammonia is dialysed, ammonium phosphate is removed; after 13 days the ratio was 82.37  $\text{Fe}_2\text{O}_3$  : 17.63  $\text{P}_2\text{O}_5$ . After another 15 days, the phosphoric anhydride amounted to 11.07 per cent., and after another 19 days, the phosphoric anhydride amounted to 9.17 per cent. The slowness of the removal of phosphoric anhydride after the first 13 days is probably due to the reformation of ferric phosphate from the double compound of ferric phosphate and ammonium phosphate which is probably present in the solution.

When the hydrogel is treated with potassium hydroxide, it is almost quantitatively converted into potassium phosphate and ferric hydroxide. When treated with potassium carbonate, a double compound is formed, soluble in water, which, when allowed to remain in solution, deposits a precipitate. When this precipitate is subjected to dialysis, it contains phosphoric anhydride and ferric oxide in the proportion 15.10 : 84.90.

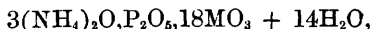
A solution of ferric phosphate in ferric sulphate, prepared by digesting normal calcium orthophosphate with a solution of ferric sulphate, and containing 130.8 grams  $\text{P}_2\text{O}_5$ , 183.54 grams  $\text{Fe}_2\text{O}_3$ , and 238.62 grams  $\text{SO}_3$  per 1000 c.c., was diluted three successive times with water; the precipitates so produced contained phosphoric anhydride and ferric oxide in the proportion 1 : 1.36. 5 c.c. of the above solution, after dilution with 900 c.c. of water, contained 3.22 per cent. of the  $\text{P}_2\text{O}_5$  originally present, 8.72 per cent. of the  $\text{Fe}_2\text{O}_3$ , and 92.62 per cent. of the  $\text{SO}_3$ .

The author points out the application of the above results to the manufacture of soluble phosphates from natural phosphates and Thomas slag.

E. C. R.

**Complex Inorganic Acids: Phosphoduodecimolybdic acid and Phospholuteomolybdic acid.** By F. KEHRMANN and E. BÖHM (*Zeit. anorg. Chem.*, 1894, **7**, 406—426).—Phosphoduodecimolybdic acid is obtained by adding a cold solution of ammonium molybdate to a cold solution of sodium phosphate and nitric acid; the precipitate thus obtained is dissolved in nitrohydrochloric acid and reprecipitated with water; finally, it is crystallised from water containing a few drops of nitric acid. It crystallises in beautiful orange octahedra, and contains by analysis phosphoric anhydride and molybdic anhydride in the proportion 1 : 23.89. The *barium salt*,  $3\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{MO}_3$ , obtained by adding barium chloride to a concentrated solution of the acid, crystallises in bright yellow octahedra, resembling the barium salt of the corresponding tungstic compound.

*Phospholuteomolybdic acid.*—The *ammonium salt*,



of this acid is obtained by precipitating with ammonium chloride the

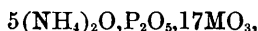
mother liquors of the barium salt of the duodeci-acid, after separating the barium therefrom with dilute sulphuric acid. It crystallises in orange-red prisms, is stable in aqueous solution at the ordinary temperature, but decomposes when heated with formation of ammonium phosphoduodecimolybdate. The *potassium salt* is obtained by adding potassium chloride to the mother liquors of the ammonium salt. It is more easily obtained by adding potassium chloride to a mixture of the duodeci-acid and phosphoric acid which has been allowed to remain for some time. It is more stable than the ammonium salt, and crystallises from boiling water without decomposition in short, orange-red prisms containing  $14\text{H}_2\text{O}$ . The *free acid*,  $3\text{H}_2\text{O}, \text{P}_2\text{O}_5, 18\text{MO}_3 + \text{Aq}$ , is obtained by adding strong alcohol to a concentrated solution of the potassium salt acidified with sulphuric acid, then adding ether, and allowing the mixture to remain in a freezing mixture until the potassium sulphate has separated. It crystallises in long, transparent, orange-red prisms, which absorb water from the air, and effloresce when allowed to remain over sulphuric acid. When the aqueous solution is treated with potassium chloride, a quantitative yield of the potassium salt is obtained.

Phosphoduodecimolybdic acid is obtained directly by adding yellow molybdic anhydride to a boiling aqueous solution of phosphoric acid. The authors attempted to prepare the corresponding arsenic compound in the same way, but the compound obtained was arsenoluteomolybdic acid. When a solution of ammonium molybdate containing nitric acid is mixed with arsenic acid in sufficient quantity for the formation of the 24-acid, a yellow precipitate of ammonium arsenoduodecimolybdate is formed. By boiling this precipitate with nitrohydrochloric acid, the luteo-acid and molybdic acid are obtained. The *ammonium salt*,  $3(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, 18\text{MO}_3 + 14\text{H}_2\text{O}$ , crystallises in beautiful, orange-red prisms, and is very soluble both in water and alcohol. The *potassium salt*,  $3\text{K}_2\text{O}, \text{As}_2\text{O}_5, 18\text{MO}_3 + 14\text{H}_2\text{O}$ , is very similar to potassium phospholuteomolybdate, and is insoluble in alcohol.

A cold, concentrated, aqueous solution of the salt,



when treated with potassium hydrogen carbonate is converted into the salt,  $5\text{K}_2\text{O}, \text{P}_2\text{O}_5, 17\text{MO}_3$  (Abstr., 1894, ii, 384). The latter forms bright, lemon-yellow crystals, decomposes slowly at ordinary temperatures, and at once on boiling. The salt,



was obtained in a similar manner in bright-yellow nodules, but owing to its instability cannot be obtained pure.

The authors give a lengthy table showing the reaction of the duodeci- and luteo-acids towards solutions of metallic salts and organic bases.

E. C. R.

**Mixed Double Haloïds of Antimony and Potassium.** By C. H. HERTY (*Amer. Chem. J.*, 1894, 16, 490—499).—The compounds

$\text{SbCl}_3\text{Br}_3\text{K}_3, 1\frac{1}{2}\text{H}_2\text{O}$ ,  $2\text{SbCl}_3\text{Br}_3\text{K}_3, 2\text{H}_2\text{O}$ , and  $\text{SbCl}_3\text{BrK}, \text{H}_2\text{O}$ , obtained by Atkinson (this Journal, 1883, 289), are in all probability not true salts, but isomorphous mixtures of the double chloride and double bromide. This view is in harmony with the observation that, after heating the supposed substance,  $\text{SbCl}_3\text{Br}_3\text{K}_3, 1\frac{1}{2}\text{H}_2\text{O}$ , until a constant weight is obtained, the residue contains an appreciable quantity of antimony, and that therefore the determination of the halogens in it by Atkinson (*loc. cit.*) affords no satisfactory evidence of the nature of the substance.

The analytical results obtained by the author point to the formulæ,  $10\text{SbCl}_3, 23\text{KCl}$  and  $10\text{SbBr}_3, 23\text{KBr}$  for the double chloride and bromide respectively, and negative the simpler formulæ,  $\text{SbCl}_3, 3\text{KCl}$  and  $\text{SbBr}_3, 3\text{KBr}$ , assigned to these compounds by Poggiale (*Compt. rend.*, 1845, 20, 1180).  
G. T. M.

**Antimony Vermilion.** By H. BAUBIGNY (*Compt. rend.*, 1894, 119, 687—690).—Antimony sulphide precipitated from solutions of the chloride by sodium thiosulphate always contains more or less antimony oxychloride, even when precipitation takes place in a strongly acid solution. The proportion of oxychloride is lower the higher the proportion of acid, and the higher the temperature at which precipitation takes place.

The precipitate obtained by the action of the thiosulphate on solutions of tartar emetic containing tartaric acid under the conditions described by Wagner, although cinnabar-red in colour, is practically pure antimony trisulphide,  $\text{Sb}_2\text{S}_3$ , whether precipitation takes place at  $80^\circ$  or at the ordinary temperature. When the dried precipitate is treated with carbon bisulphide, very little sulphur dissolves, and the precipitate is practically insoluble in tartaric acid.

C. H. B.

**Atomic Weight of Bismuth.** By R. SCHNEIDER (*J. pr. Chem.*, 1894, [2], 50, 461—471).—The author, in his earliest determinations (*Ann. Phys. Chem.*, 1851, 82, 303), found that the atomic weight of bismuth is 208 ( $\text{O} = 16$ ), and this number was confirmed by Marignac in 1883. More recently Classen (*Abstr.*, 1890, 706) has found it to be 208.9, the same method being employed as was originally used by the author. In view of this discrepancy, the experiments have been repeated with carefully purified material.

Six experiments, in which an aggregate of more than 43 grams of metal were converted into the oxide, gave as a mean result 208.05 ( $\text{O} = 16$ ), the separate numbers varying from 207.84 to 208.15. The presence of lead in the metal used, to which Classen ascribed the difference between his results and the author's, would tend to raise the number obtained, as would also any loss of bismuth during the evaporation of the solution of the metal in nitric acid and the subsequent ignition of the nitrate.

The author suggests the conversion of bismuth iodide into the oxide by ignition with mercuric oxide, or into the sulphide by treatment with mercuric sulphide, as independent methods by which further results might be obtained, but has not yet completed his experiments in these directions.  
A. H.



## Mineralogical Chemistry.

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**Origin of Bitumens.** By S. F. PECKHAM (*Amer. J. Sci.*, 1895, [3], 48, 389—395).—This paper is a retrospect of the discussion of the origin of petroleum during the 30 years that have elapsed since the author first directed his attention to the subject. The chemical theories are passed by without further notice, and the organic origin of bitumen is accepted as practically undisputed. The question to be decided is whether bitumens are distillates or whether they are indigenous in the rock formations in which they are found. The author now brings forward further evidence in support of the view he enunciated 12 years ago, that the derivation of petroleum has not been uniform. The petroleums of Ventura Co., California, he considers, were formed by distillation caused by the metamorphic action which has converted into gneiss the sandstones and shales that flank the low mountains of that region. B. H. B.

**Boleite, Cumengeite, and Percylite.** By E. MALLARD (*Jahrb. f. Min.*, 1895, i, Ref. 9—10; from *Bull. soc. fran. min.*, 1893, 16, 184—195).—Tetragonal pyramids of boleite have been prepared artificially by Friedel. Their composition is  $\text{PbCl}_2, \text{CuO}, \text{H}_2\text{O}$ , and in form they are exactly similar to the octahedral crystals previously described. The octahedral and cubic crystals originally investigated differ in composition, and the identity of the octahedral crystals with percylyte appears doubtful. The author, therefore, suggests the name of *cumengeite* for the latter crystals, and regards the birefractive portion of boleite as percylyte. B. H. B.

**Composition of Polybasite.** By G. BODLÄNDER (*Jahrb. f. Min.*, 1895, i, Mem. 98—100).—The author has analysed a specimen of polybasite from Quespisiza, in Chili, with the following results.

Ag.	Cu.	Pb.	As.	Sb.	S.	Total.
67.95	6.07	0.76	3.88	5.15	16.37	100.18

These results do not accord with the formula generally accepted,  $9\text{R}_2\text{S}, \text{Sb}_2\text{S}_3$ , the ratio being 7.74 instead of 9. B. H. B.

**Aphthalose from Vesuvius.** By P. FRANCO (*Jahrb. f. Min.*, 1895, i, Ref. 26; from *Giornale di mineralogia*, 1893, 4, 151—155).—The crystalline form of the alkali sulphate from Vesuvius was not investigated by A. Scacchi on natural crystals. The salt crusts were dissolved and recrystallised, rhombic potassium sulphate being first obtained, then rhombohedral aphthalose,  $(\text{K}, \text{Na})_2\text{SO}_4$ , and, lastly, rhombic sodium sulphate. The author has examined natural crystals from Vesuvius, and gives the results of his crystallographic measurements. B. H. B.

**Actinolite from Ouro Preto, Brazil.** By J. A. DA COSTA-SENA (*Jahrb. f. Min.*, 1895, i, Ref. 20; from *Bull. soc. fran. min.*, 1893, **16**, 206—208).—The actinolite occurring in talc schist near Ouro Preto, Brazil, exhibits the usual characteristics of that mineral. Its composition is as follows.

SiO <sub>2</sub> .	MgO.	CaO.	Na <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	Loss on ignition.	Total.	Sp. gr.
56·06	27·35	8·26	0·61	2·34	2·71	1·17	2·33	100·83	2·98

B. H. B.

**Asbestos and some Associated Minerals.** By J. T. DONALD (*Jahrb. f. Min.*, 1895, i, Ref. 21; from *Canadian Rec. Sci.*, **4**, 100—104).—The Canadian asbestos, a fibrous variety of serpentine, containing on an average 13·49 per cent. of water, occurs both in very soft and flexible portions and in hard and brittle ones. This difference appears to be due to the proportion of water, the former containing 14·05 per cent., and the latter only 12·62 per cent. In the Thetford mines, with serpentine there occur veins of a soft, white mineral (analysis I), which hardens on exposure to the air. A white, soft silicate from the serpentine of Lachute was also analysed (II) by the author.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.	CO <sub>2</sub> .	Total.
I.	43·19	1·46	0·29	—	41·52	14·00	—	100·46
II.	61·58	—	—	4·04	25·98	6·60	1·29	99·49

In addition to these, magnetite, chrome iron ore, mica, and enstatite occur in association with asbestos.

B. H. B.

**Scolecite from a Canadian Locality.** By J. T. DONALD (*Jahrb. f. Min.*, 1895, i, Ref. 25; from *Canadian Rec. Sci.*, **4**, 99—100).—Scolecite has been found in one of the granitic veins that traverse the serpentine of the Black Lake, Quebec. It occurs in transparent, acicular crystals with vitreous lustre, or in grey, white, or colourless radiated masses. On analysis it yielded

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.
46·24	26·03	14·09	13·88	100·24

B. H. B.

**Antholite from Elzivir, Colorado.** By A. P. COLEMAN (*Amer. J. Sci.*, 1895, [3], **48**, 281—283).—An asbestiform mineral occurring in large masses in the township of Elzivir has been analysed by the author. The mineral consists chiefly of irregular bundles of a strong fibrous mineral mixed with a dull green one. The latter, which resembles serpentine, has evidently been formed from enstatite, since it encloses remnants of that mineral. The results of the analyses of the fibrous mineral correspond with the composition of enstatite, supposing its constituents to be rearranged and hydrated. The correspondence is closest with some of the fibrous forms of monoclinic amphibole (antholite or kupferite).

B. H. B.

**Chocolate Nickel Ores of New Caledonia.** By T. MOORE (*Chem. News*, 1894, **70**, 279—280).—These ores, for the most part, are of no definite composition, and consist of a heterogeneous mass of various minerals, such as quartz, chromite, iron oxide, garnierite, steatite, and green nickel silicate; they are red, orange, yellow and brown, and yield, with dilute acids, a yellow iron solution containing only a little nickel, leaving a green residue. The hardness is below 1, they crumble between the fingers, and on exposure to the atmosphere fall to powder, or crack and fissure with rapidity. Before the blow-pipe, water is given off, the colour darkens, and there is either only very slight fusion at thin edges or no fusion at all.

The following analyses start with the deep chocolate-brown (1) and passing through the various shades end (6) with the ochre-yellow ore.

SiO <sub>2</sub> .	Chromite.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	NiO.	MgO.	CaO.	MnO.	H <sub>2</sub> O.
1. 33·70	1·20	19·09	1·40	31·28	3·22	0·63	0·20	9·21
2. 37·05	1·21	16·92	0·63	17·36	16·03	0·48	—	10·51
3. 24·25	0·25	42·50	—	24·58	—	0·12	0·17	8·48
4. 34·55	0·20	10·10	0·21	41·31	2·23	0·22	0·23	8·64
5. 48·25	0·62	18·40	0·10	24·67	—	0·48	—	7·33
6. 26·18	4·11	25·17	—	27·61	6·47	0·18	0·23	8·64

Metallurgically the low percentage of magnesia is a great advantage.

D. A. L.

**Mineralogical and Chemical Composition of the Sand of the Dunes of Holland.** By J. W. RETGERS (*Jahrb. f. Min.*, 1895, i, Mem. 16—74).—In this lengthy memoir, the author gives the results of his investigation of the sand of the dunes of the west coast of Holland. The minerals detected by him in this sand are the following: *Principal constituents*, quartz, garnet, augite, hornblende, tourmaline, epidote, staurolite, rutile, zircon, magnetite, ilmenite, orthoclase, calcite and apatite; *subordinate constituents*, plagioclase, microcline, cordierite, titanite, sillimanite, olivine, disthene, corundum and spinel. No mica is met with, although it has been found in sea sand. The most important result of this mineralogical investigation is the evidence afforded of the sand having been derived from the archæan crystalline schists of Scandinavia and Finland.

B. H. B.

**Serpentine of the Binnenthal.** By L. DUPARC and L. MRAZEC (*Jahrb. f. Min.*, 1895, i, Ref. 58—59; from *Bull. soc. fran. min.*, 1893, **16**, 210—217).—The serpentine of the Geissalp in the Binnenthal belongs to the gneiss of the Monte Rosa zone. Analyses yielded—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	MgO.	H <sub>2</sub> O.
38 to 40	13 to 15	32 to 34	10 to 12.

Chromium is never absent, and ferrous oxide is always present in excess of ferric oxide. Under the microscope, the following constituents are detected: hornblende, diallage, diopside, fibrous serpen-

tine, actinolite, chlorite, magnesite, and, more rarely, calcite, talc, and hæmatite. The author gives analyses of six varieties of serpentine from this locality.

B. H. B.

**The Cherts of Missouri.** By E. O. HOVEY (*Amer. J. Sci.*, 1895, [3], 48, 401—409).—The author has examined 38 specimens of chert from Missouri, about half of them being derived from the lower magnesian series, and the rest from the lower carboniferous. The microscopic characteristics of these cherts are fully described, and analysis shows that when not fossiliferous they are almost pure silica. The results of 18 analyses are given. The author's conclusion as to the origin of these cherts is that they are due to chemical precipitation, probably at the time of the deposition of the strata in which they occur or before their consolidation.

B. H. B.

**The Torda Brine Springs.** By J. NURICSAN (*Jahrb. f. Min.*, 1895, i, Ref. 67; from *Földtani Közlöny*, 1893, 23, 296—298).—The author gives analyses of water from the Roman brine spring (I) and the shaft spring (II) at Torda in Hungary. The former spring is situated north-east of Torda, 358 metres above the sea, in saliferous strata of neogene age. The temperature of the water was 23·5°, that of the air being 21°. Its sp. gr. is 1·0318 at 15°. The latter spring is situated to the north of the town, 349 metres above the sea. The temperature of the water was 23·5°, and its sp. gr. 1·0956 at 15°. One kilo. of water contains in grams—

	I.	II.	or		I.	II.
Na ....	18·2573	51·9760		NaCl .....	46·4373	131·8590
Ca ....	0·0971	0·5258		Na <sub>2</sub> SO <sub>4</sub> .....	—	0·4118
Mg ....	0·0726	0·1917		CaSO <sub>4</sub> .....	0·1224	1·7784
Fe ....	0·0029	0·0038		CaH <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ..	0·0648	—
Al ....	0·0011	0·0038		CaCl <sub>2</sub> .....	0·1276	—
Mn ....	—	trace		MgCl <sub>2</sub> .....	0·2850	0·7220
Cl ....	28·4600	80·5575		FeH <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ..	0·0089	0·0089
SO <sub>4</sub> ....	0·0873	1·5400		Al <sub>2</sub> O <sub>3</sub> .....	0·0017	0·0064
H <sub>2</sub> CO <sub>3</sub> ..	0·0571	0·0429		SiO <sub>2</sub> .....	0·0406	0·0119
SiO <sub>2</sub> ...	0·0406	0·0119		MgH <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> .	—	0·0584
	47·0760	134·8534			47·0883	134·8572

B. H. B.

**The Kolop Sulphur Spring.** By B. v. LENGYEL (*Jahrb. f. Min.*, 1895, i, Ref. 66; from *Földtani Közlöny*, 1893, 23, 293—295).—The *puszta* of Kolop is situated near Tisza Süly, in the great Hungarian plain. The spring rises in a well 14 to 15 metres in depth. In 1 kilo. of water there are contained in grams—

Na.	K.	Ca.	Mg.	Mn.	Fe.	Al <sub>2</sub> O <sub>3</sub> .	SO <sub>4</sub> .
0·9084	0·0488	0·4783	0·2813	0·0052	0·0027	0·0101	1·4199
Cl.	PO <sub>4</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> CO <sub>3</sub> .	Li, Sr, I.	Total.		
1·6670	0·0019	0·0157	0·7110	traces	5·5503		

The total quantity of free and combined carbonic anhydride is 0·7798, of free carbonic anhydride 0·2670, or 134 c.c., and of hydrogen

sulphide 0·0322, or 21 c.c. The temperature of the water is 12·8°,  
and its sp. gr. 1·0047. B. H. B.

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## Physiological Chemistry.

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**Respiratory Exchanges.** By A. LOEWY (*Pflüger's Archiv*, 1894, 58, 409—428).—The experiments referred to are numerous and were performed on a man. They relate to the differences produced in respiratory exchange by alterations in atmospheric pressure. They show that respiratory metabolism is within very wide limits not dependent on the composition of the air breathed. Increase of pressure to 1400 mm. of mercury, increase of oxygen to twice the normal, diminution of atmospheric pressure, and lessening of the oxygen until the alveolar tension is 40—45 mm. mercury do not alter the amount of gases interchanged, nor alter the respiratory quotient. With low pressures, increase of muscular work increases slightly the alveolar tension of oxygen. These facts are explicable by the compensating action of the circulation and circulating blood. Lessening of the alveolar tension below 40 mm. leads to a lessening of the oxygen taken in, an increase of the carbonic anhydride given out, and a consequent rise of the respiratory quotient.

Certain measurements are also given; the most important of which, deduced from anatomical and physiological considerations, is the capacity of the contents of the bronchial passages: it is given as between 100 and 150 c.c.

W. D. H.

**New Theory of Respiration.** By A. LOEWY and N. ZUNTZ (*Pflüger's Archiv*, 1894, 58, 511—522).—This is mainly devoted to theoretical considerations in relation to the preceding investigation and those on pp. 121, 122. The diffusion of gases on which respiration depends seems to be influenced in this way; in the blood corpuscles in large quantities, and to a less degree in the serum are non-diffusible feebly acid substances, which contain large quantities of alkali in the form of a compound which is decomposed by carbonic anhydride. One of these substances is hæmoglobin.

W. D. H.

**Behaviour of the Phosphorus of Casein in Peptic Digestion.** By E. SALKOWSKI and M. HAHN (*Pflüger's Archiv*, 1894, 59, 225—250).—This research especially relates to the behaviour of the phosphorus of casein in gastric digestion. By far the greater quantity passes into the soluble products of digestion; the remainder is in the insoluble product (paranuclein); the more favourable the conditions of digestion, the less paranuclein is obtained. The phosphorus in solution is in the form of a phosphorised albumose; the phosphorus in this is not combined as orthophosphoric acid, but by boiling with water and barium carbonate it easily passes into that condition.

Metaphosphoric acid is also absent. Paranucleic acid was obtained from the paranuclein. W. D. H.

**Amount and Composition of the Contents of the Stomach and Intestines of Rabbits at different Periods after Feeding.**

By H. WEISKE (*Landw. Versuchs-Stat.*, 1894, 45, 229—241).—Five six months old rabbits were fed for some days with oats *ad libitum*, and then for six days with 60 grams of air-dried oats each. At the end of this time the fæces seemed to consist of undigested oats, so that it could be assumed that all remains of former food had disappeared from the digestive organs. When rabbit No. 5 had finished eating on the ninth day ( $3\frac{1}{2}$  hours after the food was given), it was killed; No. 4 was killed 24 hours after it had finished eating; No. 3, 52 hours; No. 2, 97 hours; and No. 1, 160 hours afterwards. The digestive organs of all the rabbits were at once cut open and their contents separated and at once dried at  $100^{\circ}$ . The dry matter, proteids, crude fibre, ether extract, nitrogen free extract, and ash were determined in contents of the stomach and intestines, and in the fæces-balls. The results, which are given in tables, show the gradual decrease of the nutritive constituents by prolonged action of the digestive organs. Comparing the results obtained with No. 1 with those of No. 5, it is seen that the following amounts were digested: Proteids, 65.5; nitrogen free extract and fat, 72.4; crude fibre, 54.4; and ash, 47.1 per cent.

Comparing the amounts of the different constituents given in the 60 grams of oats with the amounts found in the stomach, the percentage amounts digested will be as follows. In No. 1 the stomach was practically empty.

	Dry matter.	Proteids.	Ether extract.	Crude fibre.	N. free extract.	Ash.
No. 5 ....	16.4	40.7	14.5	—	25.6	—
No. 4 ....	60.1	75.2	83.7	8.9	66.7	25.7
No. 3 ....	56.2	81.4	65.4	—	63.6	23.8
No. 2 ....	59.8	81.4	68.3	8.5	66.7	24.7

In the  $3\frac{1}{2}$  hours during which No. 5 was feeding a certain amount, chiefly protein, was digested. Most of the food was digested within 24 hours. Crude fibre does not seem to be digested or fermented to any extent, probably owing to the strong acidity of the pancreatic juice. The considerable digestion of fat cannot be explained, as neither the saliva nor the pancreatic juice digest fat as far as it is known, and no steatolytic ferment has been detected in oats.

N. H. J. M.

**Assimilation of Lime in the Body during Disease.** By v. NORDEN and K. BELGARDT (*Chem. Centr.*, 1894, i, 1005; from *Berl. klin. Woch.*, 31, 235—238).—In the course of investigations on the loss and gain of mineral matters in the body under various conditions, the following results were obtained. The lime, &c., was determined in the food and in the solid and liquid excreta. In a patient suffering from acute *arthritis deformans* and fed on milk, white bread, and butter, there was a daily gain or retention of 1.28 grams CaO, 0.06 gram MgO, and 1.13 grams  $P_2O_5$ . In a second patient, these figures

became 0.75, 0.034, and 1.13 respectively. With a patient suffering from rheumatism of the joints, the average of observations extending over a week showed a loss of 0.42 gram  $\text{CaO}$ , of 0.14  $\text{MgO}$ , and a gain of 0.42 gram  $\text{P}_2\text{O}_5$ .  
L. T. T.

**Addition of Calcium Phosphate to Food.** By H. WEISKE (*Landw. Versuchs-Stat.*, 1894, 45, 242—245).—According to the results of Neumann's experiments (*J. Landw.*, 1894, 42, 33) the addition of certain phosphates to milk for feeding calves was not only without effect in increasing the true weight but even acted injuriously owing to the increased decomposition of nitrogenous matter (compare Graffenberger, *Abstr.*, 1894, ii, 198). There was also no increased digestibility of the milk constituents. In the author's experiments (*ibid.*, 1893, ii, 132), it was shown that the effect, if any, of calcium phosphate, was rather to decrease digestibility. Calcium carbonate had no appreciable effect in Neumann's experiments; in the author's experiments, the addition of carbonate (2.5 grams per day for each rabbit) to hay seemed to diminish the digestion of the nitrogenous matter, but in the case of oats the digestibility seemed to be increased. It was pointed out that calcium carbonate might behave differently according to whether the food with which it was mixed gave an acid or an alkaline ash (*Landw. Jahrb.*, 21, 791).

N. H. J. M.

**Alkalinity of the Blood.** By C. LEHMANN (*Pflüger's Archiv*, 1894, 58, 428—461).—The passage of alkaline affinities from the blood corpuscles into the serum under the influence of carbonic anhydride is confirmed; at the same time, chlorine passes into the corpuscles from the serum. By breathing carbonic anhydride, the arterial blood of an animal becomes poorer in alkaline affinities; this is explained by the passage of the alkaline material from the plasma to the tissues and thence to the excretions. The estimation of the alkalinity of the blood by titration, and by its ability to unite chemically with carbonic anhydride, give different results. Titration gives higher results as the addition of acid liberates free alkaline affinities from the corpuscles. The long continued action of carbonic anhydride acts, however, similarly.

W. D. H.

**Alkalinity of the Blood.** By A. LOEWY (*Pflüger's Archiv*, 1894, 58, 462—507).—A research of similar nature to the foregoing. A large section treats of methods, and shows the variable results obtainable, but in blood rendered lakey the results are higher, more constant, and comparable with one another. The reason is that when the corpuscles are still intact, there is a changing relation between them and the serum. The alkalinity of the serum itself is constant, temperature making no difference. The average of the experiments recorded gives the alkalinity of the blood as 516 milligrams  $\text{NaHO}$  for 100 c.c. of blood, a higher value than in previous observations. V. Jaksch gives 200 to 300 milligrams.

W. D. H.

**Alkalinity of Fresh Blood.** By A. LOEWY and N. ZUNTZ (*Pflüger's Archiv*, 1894, 58, 507—510).—Fresh blood, kept ice-cold,



was compared, so far as its alkalinity was concerned, with some of the same blood kept at the body temperature, but tested before coagulation set in. The fresh blood has always the higher alkalinity. In order to investigate the action of coagulation, peptone was injected, but the same diminution of alkalinity was noted, although it was not quite so marked as in those specimens which still possessed the power of coagulation.

W. D. H.

**Estimation of Blood Corpuscles.** By T. LACKSCHEWITZ (*Pflüger's Archiv*, 1894, 59, 61—90). **Answer to the foregoing.** By M. BLEIBTREU (*ibid.*, 91—103; compare Abstr., 1893, ii, 331).—The first of these papers is a further criticism on Bleibtreu's method. The main points are these: on diluting the blood by intravascular infusion of physiological saline solution, the red corpuscles within the organism take up water and swell. The same must occur when, after severe bleeding, the blood is diluted by tissue juice; outside the body, either before or after coagulation, they lose this property.

The answer to this is that the experiments recorded are too few to found an opinion upon, and even these do not support the conclusions cited.

W. D. H.

**Coagulation of Milk.** By D. F. HARRIS (*J. Anat. and Physiol.*, 1894, 29, 188—200).—The differences between casein and caseinogen, as advanced by Halliburton, are insisted on. The precipitation of the caseinogen by saturation with magnesium sulphate is not due to the mechanical action of the crystals, as an inert substance like powdered glass has no precipitating effect (compare Ramsden, *Arch. Anat. Physiol.; physiol. Abth.*, 1894, 517). The scum of boiling milk consists very largely of caseinogen.

To demonstrate the presence of fat in milk, for class purposes, the blackening on adding osmic acid is recommended.

Casein can be redissolved, and it again clots with rennet; this can be repeated several times (compare Peters, this vol., ii, 80). The reasons for believing the non-identity of casein and caseinogen are as follows.

1. Decalcified milk will not coagulate with rennet, but will yield a precipitate of a proteid (caseinogen) with acid.

2. A substance can be prepared from milk by precipitation by an acid, or by saturation with a neutral salt, which, in the presence of calcic phosphate, will clot with rennet.

3. There is 13 per cent. more of calcium phosphate used up in rennet coagulation than in acid precipitation; this is an indication that these are chemically distinct processes.

4. There are also certain physical differences (cohesion, solubility, &c.) between the precipitate and the clot.

W. D. H.

**Citric acid and Calcium Phosphate in Milk.** By L. VAUDIN (*J. Pharm.*, 1894, [5], 30, 464—466).—Soxhlet has shown that milk contains citric acid. The author finds that cow's milk contains from 1 to 1.5 grams, mare's milk from 0.6 to 0.8 gram of citric acid per litre. In addition to this, milk also contains calcium phosphate in

solution, which separates out when the milk is heated, but may be redissolved if the recooled milk is agitated. Experiments made with pure calcium phosphate and pure citric acid showed that the calcium phosphate is undoubtedly held in solution by the citric acid. The author considers that the citric acid is not present in the food, but is produced in the mammary gland.

L. T. T.

**Human Blood in Disease.** By H. WENDELSTADT and L. BLEIBTREU (*Chem. Centr.*, 1894, ii, 335; from *Zeit. klin. Med.*, **25**, 204—209).—The amount of nitrogen in defibrinated blood is very variable. The highest observed percentage was in a case of Asiatic cholera (3.586 nitrogen = 22.41 grams proteid). In most cases the amount of proteid is under 20 grams per 100 c.c.; the lowest observed percentage (9.46) being in a case of cancer. The maximum percentage of nitrogen in the serum was in a case of chronic nephritis (1.336 nitrogen = 8.355 grams proteid per 100 c.c.); the next highest was in cholera (1.301 nitrogen = 8.33). The variations in the volume of the corpuscles of the blood were even greater (49.1 to 9.52 c.c. in 100 c.c. of blood).

W. D. H.

**Leucæmic Blood.** By M. MATTHES (*Chem. Centr.*, 1894, ii, 335—336; from *Berlin klin. Woch.*, **31**, 531—534).—In order to separate proteoses and peptones from blood, coagulation of the other proteids should be first effected by means of alcohol; other methods, even Devoto's, tend to the formation of proteoses during the analytical processes. In two cases of leucæmia, deuterio-albumose was formed in the serum. The serum also contained nucleo-albumin from the disintegration of corpuscles. There was no true peptone. General metabolism, except for a slight rise in the excretion of uric acid, appeared normal.

W. D. H.

**Frigotherapy.** By R. PICTET (*Compt. rend.*, 1894, **119**, 1016—1019).—The substances called bad conductors of heat, wool, cotton, silk, wood, &c., prevent very completely radiation of obscure heat emitted between  $-50^{\circ}$  and  $-60^{\circ}$ . Between  $-60^{\circ}$  and  $-80^{\circ}$  the same substances become more diathermanous, and below  $-100^{\circ}$  all the calorific radiations pass through these substances, like light traversing glass.

Experiments on dogs exposed to such temperatures, the animal being protected by warm clothing, lend support to these conclusions; the gain of appetite being taken as the chief indication of radiation. In the author's own person, he cured an attack of dyspepsia by similar means, and frigotherapy is suggested for future use in consequence.

W. D. H.

**Arrow Poisons.** By L. LEWIN (*Virchow's Archiv*, 1894, **138**, 283—346).—A continuation of a former paper (*Abstr.*, 1894, ii, 361), in which a large number more of arrow poisons, chiefly from Asia and Australasia, are treated in a similar manner.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

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**Vegetable Principles which Decompose with Liberation of Carbonic Anhydride.** By BERTHELOT and G. ANDRÉ (*Compt. rend.*, 119, 711—714).—The authors have previously shown that leaves contain substances which easily decompose with liberation of carbonic anhydride even in absence of oxygen, and other substances which oxidise readily with liberation of carbonic anhydride in volume considerably smaller than that of the oxygen absorbed (*Abstr.*, 1894, ii, 151).

Leaves dried at 110° were heated at 120—130° with a 12 per cent. aqueous solution of hydrochloric acid in an atmosphere of hydrogen. After some time, liberation of carbonic anhydride began and proceeded continuously for many hours, becoming less abundant but never ceasing altogether. It seems probable that the carbonic anhydride is derived from carbohydrates with a ketonic function, and compounds such as levulinic acid produced by their decomposition. Its production is accompanied by the formation of humic acids. The acid,  $C_{18}H_{16}O_7$ , contains an excess of hydrogen, and the production of 2 mols. of carbonic anhydride necessary for the formation of this acid would involve the destruction of about 12 times its weight of carbohydrates. When saccharose is heated with hydrochloric acid of the same concentration and under the same conditions, carbonic anhydride is liberated, although in smaller quantity, and furfuraldehyde and humic acids are formed. The behaviour of carbohydrates containing 5 or 6 atoms of carbon, or multiples of these numbers, is under investigation.

C. H. B.

**Germinating Process in *Vicia Sativa*.** By D. PRIANISCHNIKOW (*Landw. Versuchs-Stat.*, 1894, 45, 247—288).—The first series of experiments described was made with the object of ascertaining the changes in composition of etiolated plants during growth. The vetch, *Vicia sativa*, was selected, as it had already been quantitatively investigated (v. Gorup-Besanez, *Ber.*, 7 and 10; E. Schulze, *Zeit. physiol. Chem.*, 17), and because the seedlings remain healthy for a comparatively long time when kept in the dark. The material for the investigation was obtained by water-culture, the plants being examined at periods of 10, 20, 30, and 40 days after germination. The results of the analyses are given in a table, and the variations in some constituents are shown in curves. The composition of the seeds is also given for comparison. It is concluded that the loss of nitrogen during germination can be accounted for by the solution of a portion of the nitrogenous matter in the water used for softening the seeds. In the decomposition of the proteids, amido-compounds are chiefly formed, and the slight increase in the amount of phosphotungstic acid precipitate (observed in the 10-day old sprouts) is due to the production of guanidine and the liberation of choline from lecithin. As regards the amides,

asparagine is much the most prominent, and contains 60 per cent. of the total nitrogen in solution after precipitation by phosphotungstic acid. The dry matter of the axes is much more nitrogenous than that of the cotyledons, owing chiefly to the accumulation of non-proteids; they are, however, richer in proteids as well. Ammonia is only found in very small quantities (0.05, 0.04, and 0.02 per cent., 1st, 2nd, and 3rd periods respectively). In the decomposition of the starch, cane sugar is formed, and perhaps other soluble carbohydrates which do not directly reduce Fehling's solution; a directly reducing sugar occurred only in any quantity in plants of the first period of 10 days. There seems to be no relation between the decomposition of the proteids and that of the carbohydrates; most of the former disappears in the first 10 days, when the plants are still rich in carbohydrates.

In the next experiments which were made, some seedlings of *Vicia sativa* were kept for 20 days in distilled water, and others for the same period in calcium sulphate solution (1 per cent.). The effect of calcium was to increase the energy of growth, of respiration, and the decomposition of the proteids, but without any noticeable one-sided effect on the decomposition of the carbohydrates or proteids, and without altering the general character of the breaking up of the proteids (compare Bohm and Liebenberg, *Sitzungsber. k. Akad. Wiss., Wien*, 71, 1875, and 84, 1881; Raumer and Kellermann, *Landw. Versuchs-Stat.*, 25 and 29).

The last series of experiments was made with the object of comparing the composition of etiolated plants with that of normal green plants. For this purpose, the *Vicia sativa* seeds were sown in unmanured soil, and plants were taken out every three weeks for analysis. The results show that whilst, in the case of etiolated plants, the amount of asparagine increases in relation to that of other amides, it decreases in normal plants, although it remains in flowering plants in sufficient quantity to be separated. Etiolated and green plants resemble each other qualitatively, the differences are mainly quantitative (compare E. Schulze and Bosshard, *Landw. Versuchs-Stat.*, 33). N. H. J. M.

**Assimilation of Nitrates by Plants.** By DEMOUSSY (*Compt. rend.*, 1894, 119, 868—869; compare *Abstr.*, 1894, ii, 153).—The roots of a number of colza plants were immersed in 100 c.c. of an aqueous potassium nitrate solution containing 20 milligrams of nitric nitrogen. In five days the solution was almost exhausted of nitrate, whilst the water taken up was only 26 c.c., corresponding with only about 5 milligrams of nitrogen. The plants were then supplied with a fresh solution of the nitrate. In seven days they again absorbed more nitrate than corresponded with the water taken up, after which the process was reversed. Even on increasing the evaporation by exposing the plants to the air (in June), there was no further absorption of nitrate. An examination of the plants showed that more than half of the nitrate still existed as such in the plants, the rest having become transformed into proteids.

Whilst young plants from small seeds, such as colza and clover, absorb only a small amount of nitrate (9 milligrams and 6 milligrams

of nitrate respectively per 100 plants), seedlings such as maize absorb as much as 400 milligrams of nitric nitrogen per 100 plants. This absorption depends on the amount of protoplasm, since, when the cotyledons were removed from the maize plants, the absorption was reduced to 31 milligrams.

The absorption of nitrates thus depends on the amount of nitrogenous matter in the young plants; if the nitrate had been directly employed in the production of proteids necessary to the growth of the plants, the absorption would have been more active the more the proteids were wanting.

N. H. J. M.

**Foraging Powers of some Agricultural Plants for Phosphoric acid.** By W. BALENTINE (*Maine Agric. Exper. Stat. Bul.*, [2], No. 16, 1894).—Wheat, barley, maize, beans, peas, potatoes, and turnips were grown in sand (120 lbs.) contained in boxes. There were three sets in each case. Sodium nitrate (8.5 grams) and potassium chloride (2.6 grams) were applied to each box. The boxes of the first set had no phosphoric acid except that contained in the sand (0.012 per cent.); those of the second had S. Carolina rock (17 grams, containing 4.35 grams of insoluble phosphoric acid); and those of the third set acidified S. Carolina rock (28.5 grams, containing 4.46 grams of phosphoric acid three-fourths soluble).

The following amounts of dry produce were obtained (in grams).

Series.	I.	II.	III.	Series.	I.	II.	III.
Wheat ....	76.9	148.6	296.3	Beans ....	15.7	17.4	69.8
Barley ....	201.5	294.9	508.1	Peas ....	112.7	196.7	228.6
Maize .....	39.5	103.3	291.0	Potatoes..	113.3	114.6	223.6
Turnips ...	154.4	304.1	270.4				

The results show that whilst wheat, barley, maize, peas, and turnips readily appropriated the phosphates of crude, finely-ground S. Carolina rock, beans and potatoes did not. Turnips benefited most, the yield being greater than was obtained with the soluble phosphates.

The acidified rock apparently decreased the yield of barley grain, but increased the amount of straw; with wheat, both grain and straw were about equally increased.

N. H. J. M.

**Nutrition of Green Plants by Glycerol.** By E. ASSFAHL (*Ann. Agron.*, 1894, 20, 496; from Inaug. Diss., Erlangen, 1892).—Filaments of spirogyrae, deprived of starch and immersed in 0.2 per cent. aqueous glycerol, produced starch in  $2\frac{1}{2}$  hours. This was in presence of light, precautions being taken to prevent chlorophyllous assimilation. The presence of potash has some effect on the production of starch from glycerol.

N. H. J. M.

**Formation and Decomposition of Organic Acids in Higher Plants.** By K. PURJEWICZ (*Ann. Agron.*, 1894, 20, 440—446; from *Bot. Centr.*, 58, 368).—The periodic acidification and deacidification

observed in many plants has frequently been investigated, notably by Warburg, who considers acidification to be a kind of "incomplete respiration," which goes on during the night when oxygen is less abundant in the plant.

Decomposition of acids takes place under the influence of light, of higher temperature, and of prolonged darkness. It is due to total or partial oxidation—the acid disappears much less quickly in an atmosphere of hydrogen than in air. As regards the effect of increased temperature, the acids disappear very quickly at first, then more slowly. In decomposing under the influence of light, the acids may indirectly supply materials for the production of carbohydrates; this would not be the case in absence of light, when, as has been shown, the amount of carbohydrates as well as of the acids become less. Bergmann showed the production of volatile fatty acids in portions of plants kept in the dark; it is probable that these are formed by the decomposition of the more complex non-volatile acids. Experiments on the effect of light and heat on organic acids, apart from plants, showed that malic acid decomposes easily under the influence of light, whilst oxalic and tartaric acids decomposed at a temperature of 40°. This shows why deacidification takes place most readily in plants containing malic acid. Submerged plants assimilate more easily in presence of malates, tartrates, and oxalates, doubtless owing to the production of carbonic anhydride.

All plants which deacidify in presence of light become acid in the dark, but only for a certain period, after which deacidification follows. Leaves floated on 2 per cent. solutions of glucose, cane sugar, lactose, and glycerol produced more acid than when water alone was employed; the relative effect produced by the different compounds corresponding with their importance as regards production of starch (A. Meyer and Laurent). The temperature most favourable to acidification is 12–15°. The presence of oxygen is more important for the production than for the destruction of acids.

The results of experiments with *Oxalis* and with *Pelargonium* show that the ratio  $\text{CO}_2/\text{O}_2$  reaches its minimum at the temperature at which the greatest amount of acid is formed; at the temperature of 37–40°, at which the acids begin to decompose, the ratio approaches 1, or may even exceed it. Similar results were obtained when *Sedum hybridum* was kept in the dark; the ratio  $\text{CO}_2/\text{O}_2$  rose from 0.44 to 0.70 in two days, and to 1.05 in five days, whilst the acidity fell from 360 to 300.

The oxygen absorbed by plants is, as Dehérain and Moissan suppose, largely used up in the production of acids. The plants in which the acidity varies most show also the most irregular coefficient of respiration. The intensity of respiration, measured by the carbonic anhydride evolved, is least in plants showing most acidity. The reverse, however, holds good in comparing the different parts of a plant.

Further evidence in favour of these views was obtained by placing etiolated haricot seedlings in water and in 3 per cent. glucose. Under the influence of glucose there was increased acidity, and coincidentally diminished quotient of respiration:—With glucose  $\text{CO}_2/\text{O}_2 = 0.40$ , acidity = 257; with water alone  $\text{CO}_2/\text{O}_2 = 0.72$ , acidity = 185.

Ready-formed acids when given to plants may increase the destruction of acids, and consequently increase the evolution of carbonic anhydride. Etiolated wheat seedlings placed in water and in 2 per cent. calcium malate respectively for four days, and without light, gave the respiration coefficients 0.75 and 1.07. Haricots and *Sedum canescens* gave similar results.

The results (which confirm those of Warburg) show that the organic acids of plants are the products of the incomplete oxidation of carbohydrates. The evidence does not support the theory that they are the accessory products of the synthesis of proteids. The destruction of acids is a process of combustion; there are degrees of combustion which do not immediately result in the production of carbonic anhydride, but in more or less oxygenated acids. N. H. J. M.

**Mannan as a Reserve Material in the Seeds of Diospyros Kaki, L.** By J. ISHII (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 101—102).—The fruit of *Diospyros Kaki*, L. (date-plum), is largely consumed in Japan, owing to its richness in saccharine matter. When unripe, the fruit contains much tannin, which subsequently disappears. The flesh of the fruit is very rich in dextrose and levulose, but contains neither mannose nor galactose. The reserve matter of the seeds contains no starch, but consists of mannan, a polyanhydride of mannose. N. H. J. M.

**Reserve Protein in Plants.** By G. DAIKUHARA (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 77—96).—It has recently been shown that the dissolved protein in plants is not always ordinary (passive) protein, but frequently a very unstable albuminous substance (active protein). This becomes converted into the passive form when the cell dies, and in many cases during the life of the cells. The gradual disappearance of active protein from the leaves is closely connected with the production of asparagine. Thus, in leaves of *Indica glandulifera*, when kept in darkness for seven days, the percentage of asparagine rose from 0.218 to 0.606. The relation of total nitrogen to nitrogen as asparagine in leaves of *Paeonia albiflora* changed from 100 : 9.86 to 100 : 45.72 after being kept for 25 days in the dark. Various portions of a large number of plants (104 species) were examined for active protein. The substance was found in 51 plants (of 29 families); frequently in the flowers, in which case it may be absent in the leaves, or decrease in those parts nearest the flower. In *Gramineae*, active protein was only found in the seed epidermis, and only at a certain period of development. Active protein is formed in larger amounts in full sunlight than in the shade, and young leaves are richer in it than old ones. When suffering from albinism, leaves show it equally in the white as in the green parts.

N. H. J. M.

**Mucin in Plants.** By J. ISHII (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 97—100).—Whilst the animal slimes belong to the protein compounds, those hitherto found in plants are carbohydrates. The investigation of the slimy matter found in the tuberous roots of yams (*Dioscorea japonica*, Humb., and *D. batatas*, Decaigne) showed

them to contain a kind of mucin. This was prepared by Obolenski's method (*Pflüger's Archiv*, 4), and was found to possess all the essential characteristics of animal mucin; it is, however, more sparingly soluble in dilute alkalis, and yields a turbidity with potassium ferrocyanide. The percentage composition was found to be C = 52.82, H = 7.53, N = 14.20, Ash = 0.41, and O + S (by difference) = 25.05. The tubers, dried at 100°, contained 8.0 per cent. of the substance.

N. H. J. M.

**Localisation of Oxalic acid in Plants.** By R. GIESSLER (*Ann. Agron.*, 1894, 20, 446—447; from *Jena. Zeits. Naturw.*, 1893, [2], 20, 314).—The plants selected for experiment belonged to the families *Rumex*, *Oxalis*, and *Begonia*. Oxalic acid is generally found in the epidermis or in the peripheral tissues, and forms a protection against the attacks of small animals. The underground portions of the plants are, as a rule, free from oxalic acid. The leaves in particular accumulate the acid in the epidermis, the underlying tissues containing much less. Accumulations also occur in the stems and various other parts of the plants, even in the pith.

Another function of oxalic acid accumulated in the epidermis, is in relation to the function of reservoir of water served by this tissue.

N. H. J. M.

**Levulose from the Dried Peel of Citrus Aurantium Chinensis.** By B. W. BAUER (*Landw. Versuchs-Stat.*, 1894, 45, 293—294).—The dried orange peel (50 grams) was softened with acetic acid and boiled with water: 4.794 grams of crude sugar was obtained. After treatment with animal charcoal, 1.458 grams of a very hygroscopic substance was obtained,  $[\alpha]_D = -85.24^\circ$ . The rotation did not change after 24 hours. The animal charcoal employed for decolorising was covered with white rosettes of crystals.

N. H. J. M.

**Occurrence of Vanillin.** By E. O. v. LIPPMANN (*Ber.*, 1894, 27, 3409).—The author has separated vanillin from the flowers of *Nigritella suaveolens*, a variety of orchid; the extract of the plant also contains a substance recalling heliotropin or piperonal in odour.

A. R. L.

**Poisonous Action of Dicyanogen.** By O. LOEW and M. TSUKAMOTO (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 35—41).—It has been suggested by Loew (*Nat. System d. Giftwirkungen, München*, 1893) that the great stability of the proteid matter composing the living organism is caused by the simultaneous presence of aldehyde and amido-groups. If this be the case, any substance which reacts, when highly diluted, either with aldehyde or amido-groups must act poisonously on every living organism. Both dicyanogen and hydrogen cyanide should be poisonous.

A number of experiments were made to ascertain the effect of these two compounds in very dilute solution (1 : 400 to 1 : 100,000) on microbes (compare Liebig, *Annalen*, 1874, 153, 137), yeast cells, algæ (*Spirogyra communis*), phenogams (radishes, barley, lupins, and narcissus, also seeds of peas, &c.), and lastly on lower aquatic animals (nematodes, rotatoria, copepods, &c.) It was found that both dicyanogen and hydrogen cyanide are general poisons, dicyanogen



being the stronger of the two. In experiments with white rats, however, hydrogen cyanide proved to be the stronger poison, probably because dicyanogen becomes largely changed in the blood before it can reach the nervous tissues.

The author supposes that hydrogen cyanide does not poison yeast cells as such, but that it undergoes decomposition in the yeast cells before it can act poisonously. N. H. J. M.

**Poisonous Action of the Hydroxy-derivatives of Benzene on Yeast and Bacteria.** By K. YABE (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 73—75).—The poisonous effect of the hydroxy-benzenes increases generally with the number of hydroxyl-groups. The three dihydroxy-derivatives, however, differ considerably from each other in this respect, and of the tri-derivatives, phloroglucinol is less poisonous than pyrogallol.

Equivalent amounts of different phenols were dissolved in Pasteur solution and yeast added. In a second experiment, the yeast was first shaken with the solution and then kept for 70 hours; this experiment was also made with bacteria; the results, which are given in tables, show that in the case of the lower fungi, the higher hydroxy-derivatives are less poisonous than phenol itself (compare Biernacki, *Abstr.*, 1893, ii, 32; Loew, *Nat. System d. Giftwirk.*).

N. H. J. M.

**The Vegetable Cheese, Natto.** By K. YABE (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 68—72).—The vegetable cheese, natto, has been prepared in Japan since remote times. It is obtained by keeping Soja beans, previously well softened by being boiled in water, wrapped up in straw, in a well-closed, heated cellar for 24 hours. It forms a soft mass in which the beans are held together by a very thick viscous substance, and has a peculiar odour. Three micrococci (yellow, orange-yellow, and white colonies) and a bacillus, derived from the air or from the straw, were obtained from the cheese.

The following numbers show the percentage of the different forms of nitrogen in natto and in the beans from which it was prepared.

	Total nitrogen.	Nitrogen as proteids.*	Nitrogen as amides.	Nitrogen as peptone.
In Soja beans ....	7.355	6.899	0.128	0.328
In natto.....	7.542	4.033	1.892	1.617

Tyrosine, leucine, hypoxanthine and xanthine were found in the cheese; lysine, lysatinine, and arginine, which occur in germinating lupins could not be detected.

There can be no doubt that much of the peptone and also the leucine and tyrosine are products of bacteriological action. There can be hardly any doubt that the cheese is more digestible than the original beans. N. H. J. M.

**Saline Composition of Potatoes and Oats.** By PAGNOUL (*Ann. Agron.*, 1894, 20, 467—479).—Potatoes were grown in 12 pots containing each 25 litres of white sand, manured as follows:—Nitrogen (as ammonium sulphate or the nitrates of calcium, potassium, and

\* Excluding peptone.

sodium), the chlorides, phosphates, sulphates, and carbonates of calcium, potassium, and sodium, so that there were series of the three bases ( $\text{CaO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$ ) and of the four acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{CO}_3$ ), nitrogen and phosphoric acid being applied to all 12 pots. A table is given showing the produce and ash constituents obtained under the twelve different conditions. As regards the plant development, potassium had a marked effect, the average amount of dry matter being 93·4 grams as against 65·6 grams with calcium, and 55·6 grams with sodium. Sodium cannot take the place of potash, and is taken up, if at all, only in small quantity. Potassium, as well as calcium and sodium, seem to be most readily absorbed in the form of nitrate.

Oats were then grown in the same pots as were used for potatoes after they had been exposed to rain during the winter. The results are given in tables. As in the case of potatoes, potassium was the most beneficial base for oats; taking the yield of oats grown under the influence of potassium as 100, the yield with sodium was 71, and with calcium 43.

The following table shows the composition of the ash of oats (per cent. in dry matter) manured (1) with potassium, (2) sodium, and (3) calcium.

	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{CaO}$ .	$\text{P}_2\text{O}_5$ .
Potassium manure....	7·001	—	0·634	3·043
Sodium „ ....	1·192	4·585	0·682	1·983
Calcium „ ....	0·934	0·920	1·956	1·300

The results are very different from those obtained with potatoes; the potassium is higher when it is applied, whilst there is no sodium taken up under these conditions. Sodium is taken up largely when given to the plants, whilst, when the plants have to depend on the sodium and potassium originally present in the sand, the amounts of both bases taken up are about the same. The amount of phosphoric acid increases with the amount of total alkali; it is probably assimilated most readily when combined with potassium. As regards nitrogen, a comparison is made between the produce of Pot 8 (potassium nitrate and phosphate) and that of Pot 11 (ammonium sulphate, potassium phosphate, and carbonate). Whilst, at first, the plants of Pot 8 were the more vigorous, they subsequently became feeble and yellow, those of Pot 11 remaining dark green. The nitrate plants were found to be richer in total nitrogen, and much richer in nitrates than the ammonium plants, whilst the latter contained considerably more phosphoric acid. The higher amount of phosphates, possibly due to the presence of potassium carbonate, is supposed to be the chief cause of the superiority of the ammonium plants, and it is thought that the nitrate plants absorbed the nitrogen too quickly for its assimilation.

N. H. J. M.

**The Compounds of Phosphoric acid in Superphosphate Soluble in Water.** By J. STOKLASA (*Landw. Versuchs-Stat.*, 1894, 45, 161—172; compare *Abstr.*, 1891, 880, and 1893, ii, 549).—The amount of calcium carbonate was determined in the drainage from soils derived from primitive rocks and from chalk formation, and

from humus soil. The results show that a relatively large amount of carbonate is dissolved. It is estimated that the yearly loss of calcium carbonate is over 560 kilos. per hectare in the case of soils from primitive formations, and as much as 3,000 kilos. from chalky soil. The results are of interest as bearing on the loss of phosphoric acid. A litre of water saturated with carbonic anhydride, and containing calcium hydrogen carbonate (0.268 gram), held in solution 0.252 gram of  $\text{CaH}_4(\text{PO}_4)_2$ , corresponding with 0.346 gram of tricalcium phosphate, supposing this to be formed.

The total phosphoric acid of four soils is compared with the amounts of phosphoric acid found in the drainage from the soils, and the estimated loss per acre. The four soils were (1) loam from granite and gneiss formations, (2) clay from permian formation, (3) marl, and (4) humus soil.

	Loamy soil.	Clayey soil.	Marl.	Humus soil.
Total $\text{P}_2\text{O}_5$ per cent. ....	0.024	0.087	0.125	0.008
$\text{P}_2\text{O}_5$ in drainage per million	0.620	0.420	0.700	1.010
Estimated annual loss per hectare (grams) .....	13,492	9,146	15,244	21,995

The results show in a striking manner the enormous loss in the humus soil which contains the lowest percentage of phosphoric acid (compare Fleischer, *Untersuchungen üb. d. Verhalten schwerlös. Phosphate im Moorboden*, &c., *Landw. Jahrb.*, 1883, **3**, 121—201).

As regards the estimation of total phosphoric acid in soils, hydrochloric acid seems to be the most suitable solvent. Boiling nitric acid gives too high results with humus soil, owing to the oxidation of organic phosphorus compound (compare van Bemmelen, *Abstr.*, 1890, 1339, and M. Schmöger, *Ber.*, 1893, **26**, 386).

When superphosphate is treated with only a slight excess of acid so as not to completely decompose the monocalcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ , the calcium sulphate from the calcium carbonate encases the orthophosphoric acid and the untransformed tricalcium phosphate, which, in course of time, interact, forming monocalcium phosphate. Hard globules from fresh superphosphate contained, as  $\text{CaH}_4(\text{PO}_4)_2$ , 10.66 per cent. of  $\text{P}_2\text{O}_5$ ; as  $\text{H}_3\text{PO}_4$ , 7.95 per cent.; and as  $\text{Ca}_3(\text{PO}_4)_2$ , 2.06 per cent. After 60 days, the following amounts of phosphoric anhydride were found:—As  $\text{CaH}_4(\text{PO}_4)_2$ , 21.86 per cent.; as  $\text{H}_3\text{PO}_4$ , 0.59; and as  $\text{Ca}_3(\text{PO}_4)_2$ , 0.62 per cent.

Superphosphate from bone-meal containing 16.21 per cent. of phosphoric anhydride as monocalcium phosphate, and 2.43 per cent. as phosphoric acid, gave globules containing 5.01 per cent. of phosphoric anhydride as monocalcium phosphate, and 11.59 per cent. as phosphoric acid; they also contained gypsum. A filtered 1 per cent. solution deposited, after a few days, stellate groups of crystals of calcium sulphate along with a fungus, *Beggiatoa alba*. This is characteristic of superphosphate solutions, especially those of animal origin. Chloroform and carbon bisulphide prevent the separation of the crystals and the development of the organism, but the organism will vegetate in solutions of phosphates containing arsenious anhy-

dride (0.05 gram per litre) and arsenic acid (0.2 gram per litre). *Beggiatoa alba* also grows well in solutions of the beryllium and nickel salts,  $\text{BeH}_4(\text{PO}_4)_2$  and  $\text{NiH}_4(\text{PO}_4)_2$ . The production of the stellate groups of calcium sulphate crystals with the organism *Beggiatoa* only occurs in presence of phosphoric acid. The author's observations as regards the micro-organism do not agree with Winogradsky's. No hydrogen sulphide was produced from calcium sulphate in any of the cultivations. The chemistry of the fungus requires further study.

Monocalcium phosphate does not seem to react with calcium sulphate at all, and orthophosphoric acid has practically no action (compare Jones, *Landw. Versuchs-Stat.*, 13). N. H. J. M.

**Drainage from Cultivated Soils.** By P. P. DEHÉRAIN (*Ann. Agron.*, 1894, 20, 449—466; compare *Abstr.*, 1894, ii, 291).—The results obtained from March, 1893, to March, 1894, are now given. There were four fallow cases and sixteen others with grass, wheat, sugar-beet, barley, potatoes, and vines. Tables are given showing the amount of manure applied in 1893 and in 1892, the treatment of the soil—whether dug or not—the produce, and the nitrogen balance. As regards the amount of nitrates from fallow, there was much less than previously. Taking case No. 1 (without manure from commencement), the drainage in spring and summer of 1892 contained 0.158 gram per litre, in autumn and winter of 1892–93, 0.106, and in the whole year, March, 1893—March, 1894, only 0.079. Digging the soil had some effect, especially in November, but the total loss was not as great—comparing it with that from the soil left in rest—as might be expected, owing perhaps to the whole soil having been so recently disturbed in filling the cases.

The cases in which there was vegetation did not yield such large crops as previously. There was considerable loss of nitrates in the drainage from wheat, owing to the mildness of the winter having been favourable to nitrification. In two cases out of three, the loss of nitrogen in the drainage was greater than the amount found in the crop.

The losses of nitrogen from soil depend less on the abundance of crops than on the activity of nitrification, caused by climatic influence and the treatment of the soil. The loss is diminished by a good crop, partly by directly taking up the nitrates and partly by diminishing the amount of drainage.

The dry spring of 1893 was fatal to the sugar-beet, and the yield was much lower than the year before. The plants took up less nitrogen than the wheat, and there was less loss by drainage.

The vines took up but little nitrogen, and the loss by drainage was almost the same as from the fallow.

The yield of potatoes was good, and they took up in each case more nitrogen than was supplied in the manure. The losses in drainage were not great, but higher than was observed in the case of sugar-beet. Generally speaking, a good yield of sugar-beet takes up more nitrogen than potatoes, but it leaves more nitrogenous residues than potatoes, and, moreover, remains in the soil to a later period, and thus retains the considerable amount of nitrates found at this time.

The results of the experiments show what considerable losses of nitrogen there may be from fallow land—losses which nitrogen-fixing organisms cannot compensate. The practice of fallow should be discontinued.

The question as to how far the working of the soil will diminish the necessity of sodium nitrate will be next considered.

N. H. J. M.

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## Analytical Chemistry.

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**Instruments for the Graduation and Calibration of Volumetric Apparatus.** By H. N. MORSE and T. L. BLALOCK (*Amer. Chem. J.*, 16, 479—488).—The authors describe simple apparatus whereby flasks, burettes, and gas tubes may be readily verified, graduated, and calibrated. It consists of a glass vessel of known delivering capacity, with a graduated stem (to enable it to be used for graduating vessels for different temperatures), to which is attached at its lower end a Greiner and Friedrich's two-way stop-cock, which is in turn connected by a rubber tube with a supply of distilled water placed somewhat higher than the instrument itself, and also with a jet, from which the known volume of water is delivered into the vessel to be calibrated.  
G. T. M.

**Electrometric Analysis.** By R. BEHREND (*Zeit. physikal. Chem.*, 1894, 15, 498).—The author finds that all potential differences given in his previous paper (*Abstr.*, 1893, ii, 387) are too low in the ratio 1.092 : 1. Although the relative values remain unchanged, the absolute values must be altered in this proportion.  
H. C.

**Notes on Volumetric Analyses.** By B. REINITZER (*Zeit. angew. Chem.*, 1894, 547—554, 574—579).—The paper is chiefly devoted to proving the superiority of litmus over methyl-orange as an indicator. Absence of carbonic acid is, however, of great importance. Errors arising from carbonic acid in the titration of acids cannot be wholly avoided by substituting lime or baryta water for caustic alkalis, as even the former have the property of dissolving traces of calcium or barium carbonate. A warning is given as to using ordinary glass vessels for concentrating or boiling liquids which have to be titrated. For instance, in estimating the amount of alkali carbonate in mineral waters, the results may turn out quite untrustworthy, owing to the amount of alkali dissolved from the glass. Flasks made of Jena glass are, however, quite proof against the action of water.

Ammonia, obtained by distilling a known weight of pure ammonium chloride with aqueous potash, is recommended for standardising acids.  
L. DE K.

**Sensitiveness of Zone Reactions and their Use in Testing for Acids.** By H. TREY (*Zeit. anal. Chem.*, **33**, 533—543).—To avoid the troublesome neutralisation required for the qualitative detection of certain acids by silver, barium, or calcium, the author prefers the method of superposing an excess of the neutralising reagent upon the solution to be tested, and observing only the zone of contact. The usual solution, containing no other metals than those of the alkalis, is acidified with nitric acid. Then to test for phosphoric, arsenic, arsenious, chromic, oxalic, boric, sulphurous, thio-sulphuric, or silicic acids, an excess of silver nitrate is added, and any precipitate produced is removed by filtering. The perfectly clear filtrate is then carefully covered with a layer of ammonia, when any of the above acids will afford a turbidity at the zone of contact.

Another portion is treated with hydrochloric acid and barium chloride, some calcium chloride is added to the filtrate, and then a layer of sodium acetate. Here chromic, oxalic, and hydrofluoric acids give turbidity. A great advantage of the method is the sensitiveness of the reactions under these conditions. One gram-equivalent of the respective acids can be detected at the following dilutions.

By silver: boric and silicic acids in 100 litres; phosphoric, arsenic, and arsenious acids in 1,000 litres; chromic acid in 10,000 litres; oxalic acid in 100,000 litres. With barium and calcium, chromic acid gives a precipitate at 1,000 litres; oxalic and hydrofluoric acids at 100 litres. Confirmatory tests must be used to decide which of the above acids is present.

M. J. S.

**Correction in the Determination of the Titre of a Liquid holding a Precipitate in Suspension: Application to Saccharimetry.** By E. LENORLE (*Bull. Soc. Chim.*, 1894, [3], **11**, 336—343).—When a solution holding a precipitate in suspension is titrated, the result is erroneous by an amount proportional to the increase in volume of the solution caused by the precipitate. The following methods, which are of general application, enable the true results to be ascertained.

By the first method, a known volume,  $V$ , of the turbid solution is allowed to settle as much as possible, and a small quantity filtered under pressure. A known small volume,  $L$ , of the clear filtrate is titrated, and the percentage result,  $A$ , determined. The remainder of the filtrate and the precipitate are returned to the original solution, and the volume again made up to  $V$ . The operation is now repeated on this more dilute solution, with the percentage result  $B$ . Then, if  $P$  and  $S$  be the true volumes of the precipitate and solution,  $K$  the actual weight of titratable substance in the latter, and  $x$  its true percentage amount—

$$x = A_2L/V(A - B) \text{ and } K = A^2L/100(A - B).$$

A special air-pressure filter attached to a burette is used for the first filtration.

By the second method, the procedure is much the same, except that the filtration is effected through very small filters of uniform capacity

(0.5 c.c.), and the titration effected three times, the volume  $L'$  and the result  $C$  being introduced into the calculation.

$$K = \frac{AL\{B(A + B) - 2AC\}}{100\{B(A + C) - 2AC\}},$$

$$x = \frac{AL\{B(A + B) - 2AC\}}{V\{B(A + C) - 2AC\}}.$$

A modification of this method, involving the use of an air-pressure filter, is also described.

Some specimen results of the application of these methods to the polarimetric estimation of sugar in products incidental to brewing show that the correction is very considerable. JN. W.

**Estimation of Chlorine in Commercial Iodine.** By F. ULZER and A. FRIEDREICH (*Zeit. anal. Chem.*, **33**, 595—596; from *Mitt. k. k. techn. Gewerbemuseums*, 1892, 287).—Ten to twenty grams of the sample is dissolved in 100 c.c. of carbon bisulphide in a separator; 5—10 c.c. of water is added and shaken. The iodine chloride dissolves in the water, which also becomes saturated with iodine. A standard solution of potassium iodide is now run in. This, reacting with the iodine chloride, causes a liberation of iodine, which appears as a turbidity in the aqueous layer, and the addition is continued until it no longer produces turbidity. M. J. S.

**Detection of Iodine in Urine.** By A. JOLLES (*Zeit. anal. Chem.*, **33**, 543—546).—The author compares the sensitiveness of his method (Abstr., 1891, 1288), which consists in mixing 10 c.c. of the urine with an equal volume of concentrated hydrochloric acid and running 2—3 drops of a weak solution of bleaching powder down the side of the test-tube, and then adding starch solution, with that of Sandlund (Abstr., 1894, ii, 429), and finds that, although the latter is the more sensitive in aqueous solutions, this is not the case in urine. The lower limit is for Sandlund's test 0.003825 gram, and for his own 0.00153 gram of iodine in 100 c.c. After taking copaiba balsam, compounds occur in the urine which absorb iodine and impair the sensitiveness of the test. In this case, 10 c.c. of the urine is to be shaken with 5 c.c. of chloroform and filtered before testing.

For quantitative estimation, the author's method, as well as either of Sandlund's, gives satisfactory results. M. J. S.

**Estimation of Organic Sulphur.** By L. L. DE KONINCK and E. NIHOUL (*Chem. Centr.*, 1894, ii, 343; from *Mon. Scient.*, [4], **8**, 1894, 504—508).—The authors oxidise the organic substance with a mixture of calcium nitrate and calcium oxide. The combustion is done as usual in a glass tube, in the same way as the halogens are estimated. The contents of the tube are afterwards digested in dilute hydrochloric acid, and precipitated with barium chloride.

The oxidising mixture is made by dissolving 1 part of calcium nitrate in  $\frac{1}{2}$  part of water, and adding 5 parts of calcium oxide. The mixture is then thoroughly dried and powdered. L. DE K.

**Estimation of Sulphur in Volatile Organic Compounds.** By C. F. MABERY (*Amer. Chem. J.*, 1894, **16**, 544—551).—The author de-



scribes the method and apparatus he employs in the rapid determination of sulphur in petroleum. It consists of a modification of Sauer's process (this Journal, 1873, 289), improved by Burton (Abstr., 1890, 289). The combustion is effected in a stream of air supplied under pressure, and the resulting products are absorbed in a solution of sodium hydroxide of known strength, which is subsequently titrated against standard sulphuric acid.

G. T. M.

**Detection of Traces of Metallic Sulphides in Precipitated Sulphur.** By R. FRESSENIUS (*Zeit. anal. Chem.*, **33**, 573—574).—It is not unfrequent in qualitative analysis to obtain a considerable precipitate of sulphur, in which traces of the yellow sulphides of cadmium, arsenic, or tin may be present without being visible. By half filling a test-tube with the turbid mixture, adding a layer of benzene or light petroleum 2 cm. high, shaking violently for a minute, and then leaving in repose for another minute, the sulphur passes entirely into the organic solvent, whilst the sulphides are left as films, partly between the two layers of liquid, but mainly on the walls of the tube above the liquid. Should metallic sulphides be found to be present, it is best to treat a larger portion of the liquid in a similar way, and then filter the liquid through a wetted filter. After allowing the aqueous solution to drain away completely, the sulphur solution can be poured from the filter, to which the sulphides for the most part adhere firmly, and the filter can then be washed with water. Only in such exceptional cases as the decomposition of hydrogen sulphide by sulphurous or nitrous acids, is the precipitated sulphur insoluble in benzene or petroleum.

M. J. S.

**Volumetric Estimation of Sulphuric acid.** By W. WINDISH (*Chem. Centr.*, 1895, ii, 108; from *Wochschr. Brauerei*, **11**, 607—609).—*Estimation of Combined Sulphuric acid in Waters.*—100 c.c., or more, of the sample is acidified with hydrochloric acid, boiled, neutralised with ammonia, and boiled with 50 c.c. of N/15 solution of barium chloride. 50 c.c. N/50 solution of potassium chromate is then at once added, and after boiling for another minute or two the whole is rinsed into a 300-c.c. flask. After cooling, water is added up to the mark, the mixture well shaken and filtered, 100 c.c. of the filtrate is then mixed with 50 c.c. of N/50 solution of arsenious acid and 5 c.c. of 20 per cent. sulphuric acid, and after the liquid has become colourless 100 c.c. of a saturated solution of sodium hydrogen carbonate is added, then a little starch solution, and the excess of arsenious acid is titrated with N/50 solution of iodine. If  $T_1$  be the titre between the iodine and the arsenious acid,  $T_2$  the titre between arsenious acid, and potassium chromate, and  $J$  the number of c.c. of iodine solution used then—

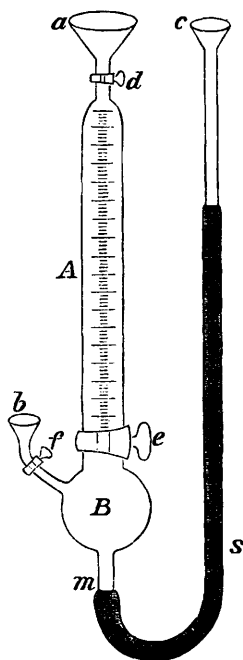
$$x = \frac{12(T_1 - J)}{T_1 - T_2} = \text{grams of SO}_3 \text{ in 100 c.c. of water.}$$

*Estimation of Sulphuric acid in Insoluble Sulphates.*—These are converted into sodium sulphate by fusing with sodium carbonate. The solution is then treated as before.

L. DE K.

**Estimation of Nitrogen in Guano.** By E. HASELOFF (*Landw. Versuchs-Stat.*, 1894, **45**, 289—292).—Twenty samples of crude and decomposed guano were analysed by the Jodlbauer and by the Ulsch-Kjeldahl methods. In some cases, both methods gave practically the same results, but in many cases the results obtained by the Ulsch-Kjeldahl method were considerably higher. In order to ascertain if these results had any relation to the amount of nitrate present, the nitric acid was separately determined in each case. The results were, however, not sufficiently definite to allow such a conclusion being drawn. The Jodlbauer method should be tested, and in the meantime the Ulsch-Kjeldahl employed.

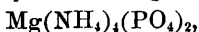
An attempt to reduce the nitrate in the guano itself by Ulsch's method, and to afterwards burn by Kjeldahl's method was unsuccessful (compare Süllwald, *Abstr.*, 1892, 528). N. H. J. M.



**New Mercury Ureometer.** By A. G. BARBERA (*Chem. Centr.*, 1894, ii, 297; from *Ann. Chim. Farm.*, **15**, 341—346).—The object of the apparatus (see illustration) is to measure the volume of nitrogen evolved by the action of alkaline hypobromite on urea. The apparatus is filled with mercury by pouring the same into the funnel *c*, after having first opened the taps *e*, *d*, and *f*. After closing the taps, a quantity of urine is put into *a*, and, after opening *d*, it is drawn into the burette *A* by lowering the tube *s*. It is then measured, the 50-c.c. burette being divided to 0.1 c.c. The funnel *b* is now filled with alkaline hypobromite, *e* is closed, and the greater part of the solution is drawn into *B* by again lowering *s*, when *f* is at once closed. The tap, *e*, is now opened, which will cause the hypobromite to ascend in the burette and mix with the urine. The liberated nitrogen is then measured as usual.

L. DE K.

**Estimation of Phosphoric acid by the Citric acid Process.** By F. GLASER (*Zeit. angew. Chem.*, 1894, 543—545).—The author has conclusively proved that when the *citrate process* is used a very large excess of magnesia mixture is essential for success. In presence of much calcium and iron, this precaution is, perhaps, superfluous, but, in most cases, when excess of magnesia fails, the precipitate is not the well-known triple phosphate, but consists more or less of a compound having the formula



which, on ignition, is converted into pyrophosphate, whilst the liberated phosphoric anhydride is volatilised.

L. DE K.

**Estimation of the Value of Phosphates insoluble in Water.**

By E. WRAPPELMEYER (*Landw. Versuchs-Stat.*, 1894, **45**, 187—194; compare Abstr., 1894, ii, 119).—With a view to ascertain which is the most suitable method for estimating the value of phosphates insoluble in water, a number of different phosphates were extracted by the methods of Jensch (5 per cent. citric acid), Scheibler (ammonium citrate with 1 per cent. of citric acid), Petermann (ammonium citrate and 1 per cent. of ammonia), and H. v. Liebig (hydrogen potassium oxalate). The total phosphoric acid was also determined in each case; Jensch's method gave too high values with most phosphorites and with basic slag, but not with Redonda phosphate. v. Liebig's method also gave high results, except in the case of the sandy Malogne (Ciply) phosphate, and basic slag. Both methods are untrustworthy. Both Scheibler's and Petermann's methods give better results, but it would be desirable to modify Petermann's method so as to make it quicker and less troublesome. Manuring experiments should be made with the various calcium phosphates, and with basic slag and phosphorites, and the results compared with those of the laboratory. It is also proposed to make vegetation experiments to ascertain the effect of species in the assimilability of phosphoric acid (compare Balentine, this vol., ii, 126). N. H. J. M.

**Analysis of Zinc Ores.**

By E. JENSCH (*Zeit. angew. Chem.*, 1894, 541—543).—The author proposes to use hydrogen peroxide instead of nitric acid to oxidise the iron in a zinc analysis. This is particularly to be recommended when the ore, or refuse, contains much manganese, as this will separate out completely with the iron when excess of ammonia is added. If the sample should contain about 5 per cent. of alumina, the precipitate must be redissolved and reprecipitated at least three times to free it from zinc. When titrating the solution with sodium sulphide, the author prefers ferric chloride as indicator. To estimate zinc oxide in weathered sulphide, the sample, which must be reduced to an extremely fine powder, is repeatedly boiled with 25 per cent. ammonia, and the united filtrates titrated.

When testing zinc ash, too much stress cannot be laid on the necessity of getting a representative sample. The author advises selecting a large sample and separating it, by means of a sieve, into several portions, each of which is then separately analysed. Some kinds of silicates contain the zinc in the form of *spinel*, when it is quite insoluble in acids, but as it is also unreducible and yields, in consequence, no metal, it need not be included in the analysis.

L. DE K.

**Rüdorff's Process of Electrolysis.**

By H. THOMÄLEN (*Chem. Zeit.*, 1894, **18**, 1121—1122).—The author's objection to Rüdorff's process (Abstr., 1893, ii, 391) is the use of Meidinger cells and the imperfect means used to ascertain the real strength of the galvanic current. The use of accumulators is recommended. L. DE K.

**Electrolytic Estimation of Copper in Ammoniacal Solution.**

By F. OETTEL (*Chem. Zeit.*, 1894, **18**, 879—881).—Although generally speaking copper is best deposited from acid solutions, still,

in the presence of chlorine, arsenic or small quantities of antimony, it will be found better to electrolyse it in an ammoniacal liquid. The presence of zinc is of no consequence, but if lead, bismuth, mercury, cadmium or nickel are present the results will be somewhat too high.

To ensure success the amount of copper should not exceed 0.8 gram per 100 c.c., and a wire-shaped positive electrode should be used. To obtain a solid deposit, the liquid should contain a large amount of ammonium nitrate, but only a slight excess of ammonia. The density of the current should be 0.07—0.27 amp. per square dm.

L. DE K.

### Indirect Volumetric Analyses by means of Sulphurous acid.

Dy D. VITALI (*Chem. Centr.*, 1894, ii, 175—176; from *Boll. Chim. Farm.*, 1894, 9).—*Estimation of Mercuric Chloride.*—The liquid, which must be neutral, is heated with sulphurous acid to 70—80° to precipitate the mercury as mercurous chloride. After filtering, the excess of sulphurous acid is expelled by heating to 60—80°, and the liberated hydrochloric acid is titrated with N/10 soda and phenolphthalein. One mol. of hydrogen chloride = 1 mol. of mercuric chloride.

*Estimation of Copper Sulphate.*—Solution of copper sulphate is mixed with excess of potassium iodide, and after adding some starch solution, sulphurous acid is slowly added until the liquid is just decolorised. The liberated sulphuric acid is then titrated with N/10 soda and phenolphthalein. 1 c.c. of soda = 0.012469 of crystallised copper sulphate. Sulphurous acid may, in turn, be estimated by means of copper sulphate.

L. DE K.

### Estimation of Iron and Aluminium in Phosphates. By V.

EDWARDS (*Chem. News*, 1894, 70, 297).—A gram of the pulverised sample is heated with ammonium citrate, at about 60°, for half an hour, filtered and washed, any cloudiness being dispelled by boiling with a little nitric acid. Citro-magnesia solution and excess of ammonia are added and well stirred in, then after two hours the phosphate precipitate is collected, washed, dried, ignited, and weighed. The filtrate is treated with ammonium sulphide, the ferrous sulphide washed, dissolved in dilute sulphuric acid, boiled, cooled, and titrated with permanganate. The aluminium is found by difference.

D. A. L.

### Volatility of Stannic Chloride. By T. M. DROWN and G. F.

ELDRIDGE (*Zeit. anal. Chem.*, 1894, 33, 598—601; from *Technology Quarterly*, 5, 136).—Solutions of stannic chloride, acidified with hydrochloric acid and heated, suffer loss of tin the more rapidly the larger the percentage of tin, the greater the amount of free acid, and the higher the temperature. A strongly acidified solution loses tin rapidly even at 100°, and by repeated evaporation with fresh acid the whole of the tin can be volatilised. 0.64 gram of tin required 5 evaporations, of 40 c.c. of strong hydrochloric acid each, on the water bath. Tin can be quantitatively separated from lead, probably from other metals also, in this way.

Solutions sufficiently dilute, or only feebly acid, may, however, be heated for some time without appreciable loss. When, by evapora-

tion, a certain degree of concentration is reached, a precipitate of a non-volatile stannic hydroxide begins to separate, and for equal degrees of acidity the concentration at which this occurs is the same, whether the evaporation has been carried on at 100° or 200°.

M. J. S.

**Estimation of Alcohol in so-called Essential Oils.** By C. FABRE, GARRIGOU, and SURRE (*Compt. rend.*, 1894, **119**, 747—748).—The usual method of estimating the alcohol in the so-called "essential oils," obtained in the manufacture of alcohol, is to agitate the oil with four successive quantities of a saturated aqueous solution of sodium chloride, remove the amyl alcohol from the latter by carbon bisulphide, distil the saline liquid, and estimate the ethylic, propylic, and isopropylic alcohols in the distillate by means of potassium permanganate.

Direct experiments on mixtures of known composition show, however, that this method only estimates from 25 to 30 per cent. of the alcohols present.

If, on the other hand, the oils are subjected to several successive series of treatments with four washings with salt solution, a much larger quantity of alcohols is extracted.

	A.	B.	C.
First series ..	8.9 per cent.	6.25 per cent.	6.2 per cent.
Second „ ..	5.4 „	3.55 „	3.8 „
Third „ ..	3.2 „	2.7 „	2.1 „
Fourth „ ..	1.9 „	1.4 „	1.15 „
Fifth „ ..	1.0 „	0.85 „	0.75 „
Sixth „ ..	0.7 „	0.45 „	0.30 „
Seventh „ ..	0.5 „	0.35 „	0.25 „
Eighth „ ..	0.25 „	0.25 „	0.20 „
	<hr/> 21.85	<hr/> 15.80	<hr/> 14.75

C. H. B.

**Estimation of Mannitol by the Optical Method.** By J. A. MULLER (*Bull. Soc. Chim.*, 1894, [3], **11**, 329—336).—Aqueous solutions of pure mannitol are practically inactive, but become more or less active in the presence of certain inorganic substances, themselves also inactive, such as borates, arsenates, &c., a solution of mannitol containing borax, for instance, being dextrogyrate. The rotatory power, moreover, of solutions containing a constant proportion of mannitol, increases with the relative amount of borax present, which must, therefore, be kept constant. The quantity used formed a nearly saturated solution. The mannitol was carefully purified. The observations were made with a Laurent polarimeter, using a tube 500 mm. long, illuminated by sodium light. The temperature of the solutions was approximately 16°, but the effect of slight alterations of temperature was negligible. In the following table of results,  $y$  = weight of mannitol in grams contained with 1.4 grams of anhydrous borax in 50 c.c. of solution at 16°,  $x$  = rotation at 16° in degrees and minutes (each the mean of three readings).

<i>y.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>
0.101	0° 20.8'	1.512	4° 1.0'
0.299	1 1.3	1.638	4 12.2
0.506	1 41.1	1.761	4 23.0
0.756	2 20.7	2.003	4 42.8
1.006	3 0.8	2.223	4 58.2
1.254	3 31.8	2.509	5 12.8
1.352	3 43.2	3.015	5 25.7

The corresponding curve closely resembles an equilateral hyperbola, but is probably composite. The increment of mannitol required to increase the rotation 10 minutes gradually increases from 0.050 gram for the first 1° 40' to 0.062 gram at 3°, 0.089 gram at 4°, 0.144 gram at 5°, and 0.465 gram at 5° 25'. Above 5°, the weight of mannitol (*y*) dissolved under the conditions specified is connected with the rotation (*x*, in minutes) caused by it by the equation  $y = \frac{43.407}{353.14 - x} + 1.433$ .

This leads to a maximum rotation of 5° 33', which no further addition of mannitol can increase. The amount of mannitol in the solution, therefore, must not be greater than 3 per cent.

To ascertain the influence on the accuracy of the process of the various substances associated with mannitol in wine, the rotatory powers of their solutions were determined before and after the addition of borax. Sodium lactate and glycerol caused no rotation in either case; the rotatory powers of rochelle salt, gum arabic, and sodium malate were slightly, that of invert sugar very considerably, increased, whilst those of dulcitol and dextrin were slightly, and those of cane sugar and glucose materially, decreased. Before estimating the mannitol in a wine, therefore, the sugars must be removed by fermentation, and the tartrates and malates by precipitation with basic lead acetate. Further, although glycerol has no rotatory power, even in the presence of borax, yet it modifies that of a borax solution of mannitol by withdrawing part of the borax from its combination with the latter; thus the rotatory power of a mannitol-borax solution was reduced from 4° 43' to 3° 46' by the addition of a quantity of glycerol, nearly equal in weight to that of the mannitol. A correction must, therefore, be made for the influence of the glycerol.

To prove the identity of the mannitol in wine with that from manna, specimens were prepared in the manner indicated above, with the addition that the products were separated from glycerol by precipitation with alcohol, decolorised with animal charcoal, and crystallised from water. They were in every respect identical with mannitol from manna.

JN. W.

**Estimation of Sugar by Fehling's Solution.** By E. NIHOUL (*Chem. Zeit.*, 1894, 18, 881—882).—The author's process (*Abstr.*, 1893, ii, 601) has been criticised by Grünhut (this vol., ii, 91), who states that neither simple roasting nor treatment with nitric acid and subsequent ignition is capable of fully converting cuprous oxide into the cupric compound.

The author has made a long series of experiments, which show the incorrectness of Grünhut's statements. L. DE K.

**Estimation of Glucose by means of Alkaline Copper Solutions.** By F. GAUD (*Compt. rend.*, 1894, **119**, 650—652).—The error in the estimation of glucose by means of alkaline copper solutions arises from secondary reactions (compare this vol., i, 163), and, if not constant, varies regularly with the concentration of the glucose solution. Accurate results can be obtained by (1) always working with glucose solutions of approximately the same strength and with constant volumes of liquid and constant temperatures, or (2) by making a correction for the error. A large number of estimations made by the author show that, with concentrations varying between 0.1 and 10.0 per 100, which are the limits met with in practice, the error  $y$  is given as a function of the exact strength  $x$ , by the expression  $y = -0.00004801 x + 0.02876359 x^2$ , or, introducing the experimental result  $\theta$ ,

$$0.02876x^2 - 1.00004801x + \theta = 0.$$

A third method is to remove the cause of the error, by substituting ammonia for sodium hydroxide. The operation must be conducted in an atmosphere of hydrogen or nitrogen, and the liquid must not be heated above 80°, or too much ammonia will be expelled from the liquid. No filtration is needed, and the completion of the reaction can be determined with great accuracy. A solution of 34.65 grams of copper sulphate in a small quantity of water, diluted to 1 litre with ordinary ammonia, gives good results. The copper can be reoxidised by means of a current of air, and the solution can be used again if a small quantity of concentrated ammonia solution is added (compare this vol., ii, 93). C. H. B.

**Analysis of Urine.** By A. HEINEBUCH (*Chem. Centr.*, 1894, ii, 115—116; from *Pharm. Centr.*, **35**, 289—290).—Fehling's solution fails to detect sugar when the amount of the latter falls below 0.05 per cent., but Boettger's test (alkaline bismuth solution) still gives a good reaction with solutions containing as little as 0.025 per cent. The most delicate reaction is obtained by the phenylhydrazine test, which detects as little as 0.01 per cent. of diabetic sugar. When using the polariscope, the urine should be decolorised with basic lead acetate, and not with animal charcoal, as this also removes some of the sugar. For the detection of albumin, the author uses the reaction with acetic acid and potassium thiocyanate, in preference to the one with acetic acid and potassium ferrocyanide. Both tests indicate as little as 0.006 per cent. of albumin, whilst the test with succinic acid and potassium ferrocyanide is only obtained with 0.007 per cent., and the nitric acid test with 0.01 per cent. L. DE K.

**Influence of Normal or Basic Lead Acetate on Invert Sugar.** By A. BORNTRÄGER (*Zeit. angew. Chem.*, 579—582).—The author has found that excess of lead acetate added to a solution of invert sugar does not, on standing, cause a diminution of sugar, but, if the mixture

is evaporated for some time, an appreciable destruction of sugar takes place.

Basic lead acetate behaves like the normal salt.

L. DE K.

**Estimation of Starch by Alcoholic Fermentation.** By A. MUNSCHE (*Chem. Centr.*, 1894, ii, 220—221, 300—301; from *Wochschr. Breuerei*, 11, 795—798, 821—824).—The sample is treated with an aqueous infusion of malt, which, at a temperature of 61—65°, will, in about half an hour, completely dissolve the starch. After cooling, some mineral phosphatic yeast food is added, also some nitrogenous food, in the shape of asparagine. After adding a weighed quantity of yeast, the liquid is put into an ordinary fermentation flask and fermented for 72 hours. Both carbonic anhydride and alcohol are estimated, but an allowance is made for the amount of these substances yielded by the malt extract itself. 51.29 parts of carbonic anhydride or 53.43 parts of alcohol correspond with 100 parts of starch.

L. DE K.

**New Process for Estimating Furfuraldehyde and Pentosans.** By C. COUNCLER (*Chem. Zeit.*, 1894, 18, 966—968).—Five grams of the sample to be tested for pentosans is distilled with dilute (12 per cent.) hydrochloric acid until the distillate no longer shows the furfuraldehyde reaction. The distillate is then diluted with the same acid to 250—500 c.c., and an aliquot part, say 20—50 c.c., is put into a stoppered flask and mixed with a not too large excess of phloroglucinol. After thorough shaking, the mixture is left for about 12 hours, the precipitate is collected on a weighed filter (dried at 98°), washed, dried at 98°, and weighed. Its weight, divided by 2.12, represents the weight of furfuraldehyde; if, however, the weight is below 0.1 gram, the factor 1.98 should be used.

The furfuraldehyde, thus found, is then calculated to pentosan, using Tollen's factor.

L. DE K.

**Estimation of Thiocyanic acid.** By J. GONDOIN (*J. Pharm.*, 1894, [5], 30, 481—484).—As copper is estimated as copper thiocyanate, the author has tried, and successfully, to estimate thiocyanic acid as this salt. The solution to be examined must be perfectly clear, and contain no free nitric acid. If free nitric acid is present, soda or potash must be added until the solution is alkaline, and this then again rendered acid with sulphurous acid. If the solution is alkaline or neutral, it should be made acid with sulphurous acid. About an equal volume of a 2 per cent. aqueous solution of sulphurous anhydride is added, and then a 10 per cent. solution of cupric sulphate, until no further precipitate is formed. The precipitate is white, the liquid green. The mixture is then heated at 80°, until the green colour just changes to blue. If the solution remains green more sulphurous acid must be added, and the whole boiled. The precipitate is collected on a tared filter, washed with hot water, dried at 100°, and weighed. Very accurate results are obtained, and the accuracy is not affected by the presence of mineral salts or cyanides.

L. T. T.



**Analysis of Milk.** By M. WEIBULL (*Chem. Zeit.*, 1894, 18, 926—928).—The author's process for the determination of the specific gravity of sour milk has been adversely criticised by Okulitsch. In reply, the author states that the process gives very satisfactory results if carried out exactly as follows:—The sample is mixed with a known volume—about one-tenth of its bulk—of ammonia, and the whole is well shaken. After about an hour, when the contents have become quite fluid, the liquid is transferred to a graduated cylinder and measured. Its specific gravity is then taken, and after allowing for the specific gravity of the ammonia and the dilution, the specific gravity of the sample is found by a simple calculation.

The fat is estimated by measuring the prepared sample in a pipette, so constructed that it will deliver exactly 7 grams of ammoniacal milk. This is then dropped on to a coil of filter-paper (Adam's process), dried and extracted with anhydrous ether. If moist ether is used, some ammonium lactate gets dissolved. The weight of fat obtained is, of course, corrected for dilution.

L. DE K.

**Detection of Margarine in Butter.** By SEYDA and WOY (*Chem. Zeit.*, 1894, 18, 906—907).—The authors criticise the three principal processes in use for the detection of margarine in butter.

*Köttstorfer's Method.*—This process, which gives the saponification number of the sample, is, of course, affected by the natural variation in the composition of butter-fat, but it is almost free from analytical errors, and, therefore, the best process as yet known.

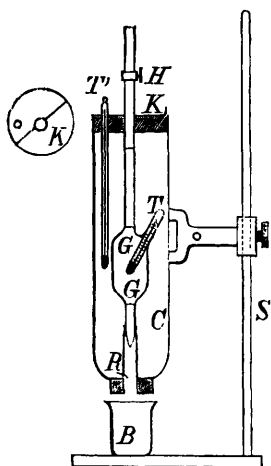
The *Reichert-Meissl Method* is based on the estimation of the volatile fatty acids. This process is liable to several analytical errors, the chief objection being that the whole of the volatile fatty acids is not collected, and it is only by exercising the greatest precautions that something like concordant results can be obtained.

*Hehner's Method.*—This process is based on the estimation of the insoluble fatty acids, and in the authors' opinion is the most complicated and untrustworthy of the three, and quite unsuited for commercial laboratories. Although the excess of mineral acid is comparatively soon washed out, the soluble fatty acids are only removed with great trouble, often necessitating a washing with 2—3 litres of boiling water. There is also great danger of serious loss by the insoluble fatty acids passing through the filter.

L. DE K.

**Testing Butter for Foreign Fats.** By C. KILLING (*Zeit. angew. Chem.*, 1894, 643—645).—The lower part of a wide glass cylinder, *C* (see next page), is closed by means of an india-rubber cork, admitting a small tube, *R*. This supports and accurately fits a 50-c.c. pipette, *G*, the lower end of which is drawn out to a point 1 mm. wide, whilst the top is provided with a stop-cock, *H*. *G* is provided with a removable thermometer, *T*, and has also two marks, one just above and another just below the bulb. At a distance of 10 cm. from the former another mark is made. The top of the cylinder is closed by a cork cut in two, one half of which admits the thermometer, *T'*. It is of the greatest importance that these thermometers should be very exact. *S* is a stand with clamps, whilst *B* is simply a beaker.

The apparatus, which is first of all tried with water at 20°, is then used for butter as follows:—The corks and thermometer *T'* are removed, the pipette is lifted out, and the thermometer, *T*, is disconnected. The sample to be tested is melted and filtered into the beaker inside a drying oven at 60°. 60 grams of clarified fat is sufficient for an experiment. In the meanwhile 1½ litres of water is heated to 43° in an enamelled saucepan, being stirred with the thermometer *T*. The butter is now placed in cold



water and stirred with *T'*, until the temperature has fallen to 40·5°. At that moment *T* is at once replaced into the bulb, the butter is drawn up by suction until it reaches the top mark, the greased stop-cock is closed and *G* connected with *R*. After placing *B* under *R*, the water, which has now cooled down to 42°, is poured down as rapidly as possible into *C*, only leaving room for the corks. As soon as both thermometers show 40°, the tap is gently opened to allow the oil to run down to the middle mark. The stop-cock is now suddenly fully opened, and the operator, having an accurate chronoscope or watch with a seconds hand at disposal, notices the exact time it takes for the oil to run down to the lower graduation. The experiment must be made three times, and

the average result recorded. The viscosity number of an oil is found by dividing the number of seconds which it takes to run through the apparatus at 40° by the number of seconds occupied by water at 20°, and multiplying the result by 100. The viscosity number of eight samples of butter varied from 276·2–281·3, average 278·5, whilst 11 samples of margarine of widely different origin gave figures varying from 313·3–317·4, average 314·7. These results being fairly constant, the author has no hesitation in recommending the taking of the viscosity number as an accurate way of estimating the amount of added solid margarine in commercial butters. If  $x$  stands for margarine and  $v$  for the viscosity number, the equation will be

$$x = (v - 278.5) \frac{100}{314.7 - 278.5}, \text{ or } x = 2.76 (v - 278.5).$$

L. DE K.

**Analysis of Lard.** By G. HALPHEN (*J. Pharm.*, 1894, [5], 30, 241–247).—In the analysis of lard, the presence of vegetable oils is readily detected by the present methods of analysis, but it is difficult to detect adulteration with beef and mutton suet. The authors find the separate determination of the iodine absorption of the separated liquid and solid acids from the lard to give good results. The liquid acids show an iodine absorption three to four times as great as that of the solid acids.

The acids are separated by Lear's method by treating them in car-

bon bisulphide solution with zinc oxide. The following table gives the results obtained.

Fat.	Iodine absorption.			Soluble zinc salts.		Liquid acids, per cent.	Solid acids, per cent.
	By 100 grams of total acids.	By 100 grams of liquid acids.	By 100 grams of solid acids.	Weight.	Colour.		
Pure American lard	63·5	91·95	28·83	64·7	amber	57·14	42·86
" French	59·0	86·61	32·91	57·83	"	50·72	49·28
American fat, A...	83·56	117·1	47·58	61·20	orange	53·86	46·14
" " B...	83·56	114·04	48·56	63·06	"	55·60	44·40
Beef suet (pressed)	17·01	75·60	12·95	7·34	amber	6·80	93·2
Mutton suet.....	37·84	80·26	17·52	35·20	"	31·44	68·56
Cotton oil.....	102·36	129·03	49·53	78·15	orange	69·06	30·96

These numbers serve not only to detect adulteration, but to form some idea of its extent and character.

L. T. T.

**Analysis of Linseed Oil.** By F. FILSINGER (*Chem. Zeit.*, 1894, **18**, 1005—1006).—The author recommends using the polariscope for the detection of rosin oil in linseed oil. Oil prepared from German or Indian seed is optically quite inactive, whilst rosin oils have a strongly right-handed polarisation.

When making an iodine absorption test, the Hübl solution should be allowed to act for 20 hours.

L. DE K.

**Analysis of Castor Oil.** By G. MORPURGO (*Chem. Centr.*, 1894, ii, 179; from *Pharm. Post*, **27**, 245).—The sample of adulterated castor oil is mixed with treble its volume of vaselin oil, and kept at 10—15°. As pure castor oil is nearly insoluble, it will, after some time, form a very distinct bottom layer, which may be measured. If seed oils are adulterated with 40—50 per cent. of castor oil di Vetere's process is recommended. The sample is agitated with half its volume of fuming hydrochloric acid when three layers are formed, the bottom layer consisting of the acid, the middle one of the castor oil more or less coloured, and the top layer containing the seed oil. To prove the identity of the castor oil, advantage may be taken of its solubility in spirits of wine. The author also recommends Draper's test:—A few drops of the oil is oxidised with about 6 drops of nitric acid, and then neutralised with sodium carbonate. If castor oil is present, the mixture emits a strong odour of ceananthic acid.

L. DE K.

**Detection of Castor Oil in Copaiba Balsam and Croton Oil.** By L. MAUPY (*Chem. Centr.*, 1894, i, 929; from *Rev. intern. falsific*, **7**, 114).—The formation of sebacic acid and caprylic alcohol when castor oil is heated with sodium hydroxide is employed for the detection of

the latter. 10 grams of the balsam, or 5 grams of croton oil, is heated in a silver basin with 10 grams of sodium hydroxide; white vapours are evolved during the whole operation, and, in presence of castor oil, the odour of caprylic alcohol is very conspicuous. When, by stirring, a homogeneous fluid paste has been obtained, 50 c.c. of water is added, and the solution filtered hot through a wetted double filter in a hot-water jacket. Sebacic acid is then thrown down from the filtrate on the addition of a mineral acid.

M. J. S.

**Application of Gas Analysis to Cheese-making.** By M. SCHAFFER (*Staz. Sper. Agrar.*, 1894, 26, 32—47; from *Landw. Jahrb. d. Schweiz.* 1893, 7, 72).—The presence of micro-organisms being an important point in cheese-making, and their isolation and identification a process too difficult and laborious for general use, the author has devised a method by means of which the presence of the particular ferment which causes swelling in cheese can be detected, and its relative amount ascertained. This is done by keeping the milk at a temperature of 38°, and collecting and measuring the gas evolved in a given time. The apparatus consists of a cylindrical vessel (100 c.c. capacity) connected, by means of a narrow tube bent four times, with the lower end of an upright graduated tube. This has at its lower end a second (outlet) tube, which is bent upwards a little and terminates in a bulb. The upper end of the measuring tube is provided with a tap. When used, the apparatus is first sterilised; the lower vessel is then filled with milk (100 c.c.), the upper vessel with an antiseptic liquid coloured with magenta and acidified with sulphuric acid (0.5 per cent.). The two portions of the apparatus are connected and placed in a Walther fermentation apparatus kept at 38°. The gas, if produced, rises into the measuring tube, the water so displaced flowing into the bulb.

A number of experiments were made with milk, rennet, and sterilised milk diluted with water from various sources; and the results are given in tables. One sample of milk, infected with *Guillebau a* (a bacillus known to produce the swelling of cheese), gave 82 c.c. of gas, or 82 per cent. by volume, after 24 hours. Milk which produces 10 per cent. of gas in 12 hours would doubtless cause the cheese to swell. All the samples of rennet gave more or less gas, showing how important it is that rennet should be prepared with more care than is usual. The samples of water used in diluting the milk of the third series of experiments were analysed. There seemed to be no very definite relation between their chemical composition and the amount of gas they caused to be given off by the milk. Most of them produced gas (compare E. v. Freudenreich, *J. Board of Agric.*, 1894, 1, 68).

N. H. J. M.

## General and Physical Chemistry.

**Superposing of the Optical Effects of Different Asymmetric Carbon Atoms in the same Active Molecule.** By PHILLIPE A. GUYE and M. GAUTIER (*Compt. rend.*, 1894, **119**, 740—743).—The authors advance the two following theories, with reference to the effects due to different asymmetric carbon atoms in the same active molecule.

1. In any molecule containing several asymmetric carbon atoms, each one behaves as though the rest of the molecule was inactive.

2. The optical effects of the different asymmetric carbon atoms may be summed algebraically.

From these principles, it follows that the rotatory power of a substance containing several asymmetric carbon atoms may be obtained by ascertaining the effect due to each atom, as if the rest of the molecule was inactive, and then taking the sum of the several effects.

This the authors have done for the amylic oxide  $(\text{CHMeEt}\cdot\text{CH}_2)_2\text{O}$ , the results actually obtained being in accordance with the theory.

H. C.

**Optical Rotation of Amyl Derivatives.** By PAUL WALDEN (*Zeit. physikal. Chem.*, 1894, **15**, 638—655).—In order to test the validity of

Compounds.	$m_D$ .	Spec. rot.	Mol. rot.
Amylactic acid, $\text{Ay}\cdot\text{CH}_2\cdot\text{COOH}$ .....	73·0	+ 8·53	11·08
Amylic acetate, $\text{CH}_3\cdot\text{COOAy}$ .....	73·0	2·50	3·25
Amylic bromide, $\text{AyBr}$ .....	94·0	3·50	5·29
Amylpiperidine, $\text{C}_5\text{NH}_{10}\text{Ay}$ .....	98·0	7·94	12·31
Ethylic amyliacetate, $\text{Ay}\cdot\text{CH}_2\cdot\text{COOEt}$ .....	101·0	6·56	10·37
Amylic butyrate, $\text{C}_3\text{H}_7\cdot\text{COOAy}$ .....	101·0	2·97	4·69
Amylic isobutyrate, $\text{CHMe}_2\cdot\text{COOAy}$ .....	101·0	2·83	4·47
Amylic chloracetate, $\text{CH}_2\text{Cl}\cdot\text{COOAy}$ .....	107·5	3·16	5·20
Amylmalonic acid, $\text{Ay}\cdot\text{CH}(\text{COOH})_2$ .....	117·0	5·25	9·13
Ethylic amyliacetoacetate, $\text{COMe}\cdot\text{CHAy}\cdot\text{COOEt}$ ..	143·0	12·14	24·28
Amylic iodide, $\text{AyI}$ .....	141·0	4·55	9·00
Amylic bromobutyrate, $\text{CHEtBr}\cdot\text{COOAy}$ .....	180·0	2·27	5·38
Amylic isobromobutyrate, $\text{CBrMe}_2\cdot\text{COOAy}$ .....	180·0	2·53	6·00
Diethylic amyilmalonate, $\text{Ay}\cdot\text{CH}(\text{COOEt})_2$ .....	173·0	10·14	23·32
Diethylic paranitrobenzylamyilmalonate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CAy}(\text{COOEt})_2$	308·0	1·25	4·56
Diamylactic acid, $\text{CHAy}_2\cdot\text{COOH}$ .....	143·0	18·27	36·54
Amylic amyliacetate, $\text{Ay}\cdot\text{CH}_2\cdot\text{COOAy}$ .....	143·0	7·01	14·02
Ethylic diamylacetate, $\text{CHAy}_2\cdot\text{COOEt}$ .....	171·0	17·99	41·01
Diamylic oxalate, $\text{C}_2\text{O}_4\text{Ay}_2$ .....	173·0	4·93	11·35
Diamylic fumarate, $\text{C}_4\text{H}_2(\text{COOAy})_2$ .....	199·0	5·69	14·56
Diamylic maleate, $\text{C}_4\text{H}_2(\text{COOAy})_2$ .....	199·0	4·35	11·13
Ethylic diamylacetoacetate, $\text{COMe}\cdot\text{CAy}_2\cdot\text{COOEt}$ ..	213·0	$\pm 0\cdot00$	0·00
Diamylic chlorofumarate, $\text{COOAy}\cdot\text{CH}\cdot\text{CCl}\cdot\text{COOAy}$	233·5	+ 5·74	16·67
Diamylic chloromaleate, $\text{COOAy}\cdot\text{CH}\cdot\text{CCl}\cdot\text{COOAy}$	233·5	4·60	13·36
Diethylic diamylmalonate, $\text{CAy}_2(\text{COOEt})_2$ .....	243·0	5·82	17·46
Diamylic phthalate, $\text{C}_6\text{H}_4(\text{COOAy})_2$ .....	249·0	3·88	11·87
Amylic diamylacetate, $\text{CHAy}_2\cdot\text{COOAy}$ .....	213·0	13·96	37·10

Guye's hypothesis, the author determined the rotation of a large number of compounds obtained from active amylic alcohol. The alcohol employed for the purpose had the specific rotation  $[\alpha]_D = -4.78$ . The weights of the groups in combination with the asymmetric carbon are respectively 1, 15, 29, and  $m_1$ , the value of the last variable being given in the third column of the accompanying table which embodies the results of the researches,  $A_y$  representing the active amyl radical  $\text{CHMeEt}\cdot\text{CH}_2$ .

From these, the author concludes that a constant increase in the weight  $m_1$  may correspond with a decrease as well as an increase in the mol. rotation; that the rotation is largely dependent on the nature of the combined groups; metameric compounds possessing different rotations, and the same obtaining for stereoisomerides. Of isomeric compounds, that one has the greater rotation in which the oxygen aggregate is the farther removed from the asymmetric carbon atom; the presence of a second active radical may correspond with either an increase or decrease in the rotation.

L. M. J.

**Action of the Cathode Discharge on some Salts.** By EUGEN GOLDSTEIN (*Ann. Phys. Chem.*, 1894, [2], 54, 371—380).—The cathode discharge causes phosphorescence in many substances, and the author finds that several of these at the same time undergo remarkable changes. Thus lithium chloride, the phosphorescence of which is of an intense bright blue, changes in a short time from white to a heliotrope or dark violet colour, the phosphorescence at the same time becoming fainter. If the tube containing the salt is vacuous or filled with dry air, the coloration is permanent, but when the tube is opened and ordinary air admitted, the salt again becomes colourless. If the coloured salt is gently heated, the dark violet changes to a brown, but when strongly heated, the salt becomes colourless. The chlorides of sodium and potassium give rise to similar phenomena, as do also potassium iodide and carbonate, lithium bromide and iodide, sodium bromide and rubidium iodide. The author considers that the changes are due to a physical modification and not to chemical change in the substances in question.

H. C.

**Condensation of Electrolytic Gas by Porous Substances, especially by Metals of the Platinum Group.** By LOUIS P. CAILLETET and EMMANUEL COLLARDEAU (*Compt. rend.*, 1894, 119, 830—834; and by MARCELLIN BERTHELOT, *ibid.*, 834).—Spongy platinum was enclosed in two small silk bags, together with a platinum wire to serve as a conductor, and immersed in dilute sulphuric acid (1:10), one bag forming the anode and the other the cathode. An electric current was allowed to pass until the platinum was presumably saturated with the two gases, and the two bags were then placed in electrical communication so as to form a gas battery similar to that of Grove. Under these conditions, a much more powerful and persistent current is obtained than with the same weight of platinum in the ordinary metallic condition, and the duration of the current is greatly increased under pressure.

Under atmospheric pressure, the discharge lasts only about 10 seconds and the E.M.F. falls continuously from 1.8 volts to zero.

Under gradually increasing pressure, the manner of discharge gradually alters and three periods are recognisable. There is first a period of very rapid fall in the intensity of the current, which afterwards rises slightly; this is followed by a period of constant intensity, the intensity slightly increasing with the pressure, and the E.M.F. being about 1 volt; finally there is a period of fall less rapid than the first. The capacity of the accumulator thus formed by the spongy platinum is 56 ampère-hours per kilo. of metal under a pressure of 580 atmos., and the intensity of the current may easily reach 100 ampères per kilo. In order to obtain the best results, about three times as much platinum should be used for the negative pole as for the positive. The yield of the accumulator is as high as 95 or even 98 per cent. provided that the charge is not pushed to its limit, and that the discharge begins immediately after charging.

Iridium behaves like platinum; ruthenium is slightly attacked at the positive pole, but will also form an accumulator with a capacity that increases with the pressure, but with an E.M.F. that is not constant but decreases continuously from 1.6 volts to zero, whatever the pressure.

Palladium in the metallic form constitutes an accumulator of very feeble capacity, owing to the rapidity with which it is saturated by oxygen, but in a spongy condition, it gives results much better than those obtained with any other metal of the platinum group, and even under atmospheric pressure is equal to platinum under a pressure of 20 to 30 atmos. As the pressure increases, the phenomena are similar to those observed with platinum, but the capacity of the accumulator is three or four times as great, and under a pressure of 600 atmos. may reach 176 ampère-hours per kilo.

Gold precipitated by sulphurous acid behaves like the platinum metals, but the capacity is lower and the intensity of the current varies somewhat differently.

Silver, tin, nickel, cobalt, and carbon, undergo change at the positive pole, and although there is some accumulation of electrical energy, it is not affected by pressure and seems to be due to chemical changes.

Berthelot points out that platinum, palladium, and analogous metals form definite compounds with oxygen, and especially with hydrogen, at the ordinary temperature, their formation being influenced by pressure.

C. H. B.

**Limits of Electrolysis.** By MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1894, [7], 3, 138—144).—The author has formerly shown by experiment that in the electrolysis of an alkali salt, of which neither the acid nor base is oxidised or reduced during the operation, the minimum E.M.F. necessary for electrolysis is the sum of two equivalent quantities, the one being the heat absorbed in the separation of the acid and the base in dilute solution, the other the heat of decomposition into oxygen and hydrogen of the water holding the substance in solution. In the case, for instance, of potassium sulphate in dilute solution, the sum of the two quantities of heat is

$$15.7 + 34.5 = 50.2 \text{ Cal.},$$

when 1 gram of hydrogen is liberated. This is equivalent to 2.20

volts, a number which Le Blanc has obtained by direct observation. Other results are quoted in support of the above law, which the author maintains as an empirical law, independent of any hypothesis regarding the condition of the dissolved salts in solution. H. C.

**Thermoelectric Phenomena between Two Electrolytes.** By HENRI BAGARD (*Ann. Chim. Phys.*, 1894, [7], 3, 83—138).—In continuation of his researches (Abstr., 1892, 1037, and 1893, ii, 202), the author has determined the thermoelectric E.M.F. in the cases of a number of couples consisting of two electrolytes. The E.M.F. is in all cases, as with the metals, a function of the second degree of the temperature, and very frequently the existence of a neutral point was observed somewhere between 0° and 75°, the limits of temperature of the experiments. In the case of two solutions of the same salt of different degrees of concentrations, the current always travels across the heated junction from the dilute to the concentrated solution. Becquerel's law of intermediate substances, and the law of intermediate temperatures are found to hold good. There is a simultaneous inversion of the thermoelectric E.M.F. and of the Peltier effect at the point of contact of the two electrolytes, and an electrical transference of heat in these liquids.

H. C.

**Thermoelectric Properties of Platinoid and Manganine.** By BENJAMIN O. PEIRCE (*Amer. J. Sci.*, 1894, [3], 48, 302—306).—The author has had occasion to determine the thermoelectric relations of copper to such platinoid and manganine as are to be obtained in the market. The nature of the results will be seen from the following table. The current passes across the hot junction from the first named metal to the second; the E.M.F. is measured in microvolts.

Temperatures of the junctions.	E.M.F.	
	Copper vs. manganine.	Platinoid vs. copper.
0° and 10°	4·3	189
0    "   20	9·2	379
0    "   30	14·1	572
0    "   40	19·6	769
0    "   50	25·7	971
0    "   60	32·6	1179
0    "   70	40·2	1391
0    "   80	48·1	1609
0    "   90	56·4	1834
0    " 100	64·9	2063

The results vary with the thickness of the wires used and the annealing of the metals, but the E.M.F. of no one of the manganine-copper combinations experimented on was greater than about one-seventh that of the weakest of the platinoid-copper combinations under similar circumstances. Hard drawn manganine wire can be used with advantage as a slide wire, since accidental heating does not alter its resistance appreciably, and the thermoelectric effects at the junctions of the slider would be insensible.

H. C.



**Influence of Magnetism on Chemical Action.** By F. A. WOLFF, jun. (*Amer. Chem. J.*, 1895, 17, 122—138).—In 1881, Remsen noticed that when copper is deposited from a solution of copper sulphate on a plate of iron placed on the poles of a magnet, it is arranged in ridges round the poles which are at right angles to the lines of force and consequently coincident with the lines marking the equipotential surfaces. The outlines of the poles of the magnet are always sharply defined on the plate, as along these lines a portion of the iron of greater or less width is left unacted on. The author has investigated these phenomena, and his results and conclusions are contained in this paper. The absence of deposit over the outlines of the pole is not due to any direct influence of magnetism on chemical action, but to the accumulation of the iron salts formed in the reaction about those parts, and to the electric currents arising therefrom. The fact that the deposit is thickest immediately adjoining the protected region also finds its explanation in the electrolysis accompanying these currents. The deposition in ridges is not due to any direct influence of magnetism on chemical action, and is not directly due to the voltaic currents in the liquid. Copper is deposited in ridges on both magnetic and non-magnetic metal when a solution of copper sulphate is allowed to flow over them and the ridges are arranged along the lines of flow. The deposition in ridges when copper is deposited on iron in a magnetic field may be due to similar action.

H. C.

**Formula of van der Waals:**  $\log p_c - \log p = f T_c/T - f$ . By PHILIPPE A. GUYE (*Chem. Centr.*, 1894, ii, 8; from *Arch. Sci. Phys., Genève*, [3], 31, 463—480).—Van der Waals expresses the relationship of the vapour pressure to the temperature by the formula  $\log p_c - \log p = f T_c/T - f$ , where  $T_c$  is the absolute critical temperature,  $p_c$  the critical pressure,  $p$  the vapour pressure at any other temperature  $T$ , and  $f$  a constant. The numerous vapour pressure determinations that have been made in recent times have enabled the author to submit this relationship to a new and thorough examination. It is found that those liquids in which, according to the investigations of Ramsay and Shields, complex molecules are present, must be considered apart from those in which only simple molecules occur. Substances of the latter order give values for the constant  $f$  which vary but slightly from a certain mean value. Thus, for benzene, the values lie between 2.827 and 2.976, and for carbon tetrachloride from 2.753 to 3.022. The mean value for the constant with liquids containing simple molecules is 3.06. Liquids which approximate to this are benzene, chloroform, carbon and tin tetrachlorides; ether, fluorobenzene, methylic, ethylic, and propylic formates, acetates and propionates; methylic butyrate and isobutyrate. Variations of the values calculated for  $f$  from the mean may perhaps be referred to inaccuracies in the data for the critical constants.

With liquids, the molecules of which are probably polymerised, the value obtained for  $f$  no longer approximates to a constant mean value, but is found to be continually decreasing with rising temperature. Thus, ethylic alcohol gives the value 4.024 at 0°, and

3.576 at 230°. The values of  $f$  for these liquids are greater than 3.07. The smallest values are methylic alcohol, 3.557; ethylic alcohol, 3.576; propylic alcohol, 3.494; acetic acid, 3.385 (compare this vol., ii, p. 99).

H. C.

**Law of Corresponding Boiling Points.** By ULRICH DÜHRING (*Ber.*, 1895, **28**, 366—367).—The author proposes soon to reply at length to the criticism of his law which has been published recently (this vol., ii, 70).

A. H.

**Mercuric Nitrates.** By RAOUL VARET (*Compt. rend.*, 1894, **119**, 797—799).—Determinations of the heat of dissolution of mercuric nitrate in nitric acid give the following results.

$\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$ sol. + $4\text{HNO}_3$ (1 mol. = 1 litre)	
at 16° .....	absorbs -0.71 Cal.
$2[\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}]$ sol. + $4\text{HNO}_3$ (1 mol. =	
1 litre) at 16° .....	„ -1.42 „

From the action of hydrochloric acid on mercuric nitrate and of nitric acid on mercuric chloride, of hydrocyanic acid on mercuric nitrate and nitric acid on mercuric cyanide, of mercuric nitrate on sodium chloride, and sodium nitrate on mercuric chloride, it follows that

$\text{HgO}$ ppt. + $2\text{HNO}_3$ dil. = $\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$	
sol. + $\text{H}_2\text{O}$ liq. ....	develops + 7.36 Cal.
$\text{Hg}$ liq. + $\text{N}_2$ gas + $\text{O}_6$ gas + $\frac{1}{2}\text{H}_2\text{O}$ liq. =	
$\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$ sol. ....	„ + 58.36 „

*Basic Mercuric Nitrate.*—Heat of dissolution in dilute nitric acid + 3.8 Cal. Methods similar to those employed in the case of normal nitrate show that

$3\text{HgO}$ ppt. + $2\text{HNO}_3$ dil. = $3\text{HgO}, \text{N}_2\text{O}_5, \text{H}_2\text{O}$	
liq. ....	develops + 15.45 Cal.
$\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$ sol. + $2\text{HgO}$ + $\frac{1}{2}\text{H}_2\text{O}$ liq.	
= $3\text{HgO}, \text{N}_2\text{O}_5, \text{H}_2\text{O}$ sol. ....	„ + 8.09 „

The action of a large quantity of water on normal mercuric nitrate only very partially converts it into the basic salt;  $\text{Hg}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$  sol. +  $\text{H}_2\text{O}$ , 10 litres =  $\frac{1}{18}\text{Hg}(\text{NO}_3)_2$  diss. +  $\frac{2}{18}\text{HNO}_3$  diss. +  $\frac{1}{18}(3\text{HgO}, \text{N}_2\text{O}_5, \text{H}_2\text{O})$  sol. absorbs - 1.2 Cal.; complete conversion into basic nitrate would absorb - 2.21 Cal., and the dissolution of the basic nitrate in excess of acid would develop 1.26 Cal. The least endothermic reaction corresponds with the formation of a solution containing free nitric acid and saturated with the basic nitrate.

Nitric acid is practically completely displaced from its combination with mercury by hydrocyanic and hydrochloric acids (compare this vol., ii, 103).

C. H. B.

**Determination of Molecular Weights. I.** By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1894, **15**, 656—680).—The author gives an account and criticism of the various forms of apparatus employed by himself and other observers in the determination of molecular

weights by the boiling point method. The boiling tube is first described and compared with those of Raoult, Lespieau and Sakurai; various forms of jacketing vessels, usually of porcelain, are described as well as the condensers and burners generally employed. The method of inserting the substance into the tube is explained and some details in connection with the use of the Beckmann thermometer are given, a table of the values of one scale division at different temperatures being also added. The effects of alterations in the atmospheric pressure are shortly discussed, and the paper, which is illustrated by numerous woodcuts, concludes with a short claim for priority in the employment of certain of the forms of instruments described.

L. M. J.

**Freezing Points of Mixtures of Alcohol and Water.** By RAOUL PICTET (*Compt. rend.*, 1894, **119**, 678—682).—The author's results of the determination of the freezing points of mixtures of ethylic alcohol and water are contained in the following table.

Hydrates.	Sp. gr.	Per cent. alcohol.	Freezing point.
$C_2H_5O + H_2O$	0.8671	71.9	—51.3°
„ $2H_2O$	0.9047	56.1	—41.0
„ $3H_2O$	0.9270	46.3	—33.9
„ $4H_2O$	0.9417	39.0	—28.7
„ $5H_2O$	0.9512	33.8	—23.6
„ $6H_2O$	0.9578	29.9	—18.9
„ $7H_2O$	0.9627	26.7	—16.0
„ $8H_2O$	0.9662	24.2	—14.0
„ $9H_2O$	0.9689	22.1	—12.2
„ $10H_2O$	0.9712	20.3	—10.6
„ $11H_2O$	0.9732	18.8	—9.4
„ $12H_2O$	0.9747	17.5	—8.7
„ $13H_2O$	0.9761	16.4	—7.5
„ $16H_2O$	0.9793	13.8	—6.1
„ $20H_2O$	0.9824	11.3	—5.0
„ $35H_2O$	0.9870	6.8	—3.0
„ $50H_2O$	0.9916	4.8	—2.0
„ $100H_2O$	0.9962	2.5	—1.0

H. C.

**Freezing Point of Dilute Solutions.** By WALTHER NERNST and RICHARD ABEGG (*Zeit. physikal. Chem.*, 1894, **15**, 681—693).—If the solutions could be adiabatically enclosed, the temperature would approximate towards the true freezing point,  $T_0$ , of the solution, and the rate of change of temperature might be considered as given by the equation  $dt = K(T_0 - t)dz$  ( $z$  = time). Owing, however, to exchange of heat with the surrounding objects, the temperature tends towards a limit  $t_0$ , and the course of temperature change would be represented by  $dt = k(t_0 - t)dz$ . By combining these two equations, we obtain  $dt = [K(T_0 - t) + k(t_0 - t)]dz$ , and hence, by equating to zero, the final temperature  $t_1 = T_0 - k/K(t' - t_0)$ . This is the temperature observed in the freezing point observations, and differs from  $T_0$  by an amount dependent on  $t_0 - T_0$  and the magnitude of  $K$ .

Experiments were then undertaken on the freezing points of solutions of sodium chloride, ethylic alcohol, and cane sugar, previous experiments having been made in each case to obtain the values of  $k/K$  and  $t_0$ . In the case of sodium chloride solutions, the correction is so small as to be negligible, and the results of the author, of Jones, and of Loomis, show excellent agreement. In the case of cane sugar, however, the correction is no longer negligible, reaching, in some cases,  $0.006^\circ$ . The results, uncorrected and corrected, are contained in the table.

$t$ .	$t$ (corr.).	$m$ .	$t/m$ .	$t/m$ (corr.).
0.0277	0.0337	0.0178	1.55	1.88
0.0612	0.0634	0.0353	1.73	1.79
0.1222	0.1247	0.0688	1.78	1.81
0.2410	0.2450	0.1305	1.85	1.88

The values for  $t/m$  so obtained are constant to within experimental limits. To further test these views, a jacket at  $-2.7^\circ$  was used, whereby  $t_0 < t_1$ ; the value for  $t(\text{corr.})/m$  so obtained is 1.86. The high results of Arrhenius, Raoult, and Jones are, in all probability, due to the use of a jacket at a much lower temperature than the freezing point of the solution.

L. M. J.

#### Cryoscopic Researches on Alkali Aluminates and Borates.

By ARTHUR A. NOYES and W. R. WHITNEY (*Zeit. physikal. Chem.*, 1894, 15, 694—698).—The authors first determined the lowering of the freezing point caused by dissolving aluminium in alkali solutions, employing for the purpose the ordinary Beckmann apparatus. The freezing point of the alkali is not noticeably altered, hence the composition of the aluminate must be represented by  $\text{MAlO}_2$ , the aluminium being trivalent. For the examination of borates, alkali solutions were prepared and boric acid added. In the more dilute solution, no lowering occurred until the boric acid and alkali were present in molecular ratio; a slight increase being observed in the stronger solutions. The borates formed must hence correspond with the formula  $\text{MBO}_2$  or  $\text{MH}_2\text{BO}_3$ . Addition of a second molecule of boric acid caused a diminution of the lowering to about three-fourths the original value, further addition producing no further effect. This, the author considers, is due to the formation of complex salts containing 2 potash and 4 boric acid molecules, which dissociate into 2 potassium and 1 complex acid ion, that is,  $\text{M}_2\text{B}_4\text{O}_7$ , whilst other boric acid molecules attach themselves to the acid radicle and consequently produce no effect on the freezing point.

L. M. J.

#### Solubility of Solid Non-electrolytes in Mixtures of Ethylic

Alcohol and Water. By ARNOLD F. HOLLEMAN and A. C. ANTUSCH (*Rec. Trav. Chim.*, 1894, 13, 277—306).—Bodländer (*Abstr.*, 1891, 794), from a study of the solubility of substances in mixtures of water and alcohol, concludes that  $W/\sqrt{S} = \text{const.}$ , where  $W$  is the quantity of alcohol contained in a given volume of the solution, and  $S$  the quantity of the dissolved substance in the same volume. The authors

have examined the solubilities of the following substances in mixtures in all proportions of alcohol and water:—Paracetotoluidide,  $\alpha$ -acetophthalide, phenylthiocarbamide, benzoylphenylhydrazine, triphenylguanidine, acetanilide, benzamide, trinitrobenzene, and alanine. They find that Bodländer's formula does not hold for their results. In all cases, except that of alanine, which is more soluble in water than in alcohol, the compounds dissolve to a greater extent in alcohol than in water. On the addition of water to the alcohol, the solubility usually at first undergoes a marked increase, a maximum is reached, and then the solubility decreases. In a few cases, the preliminary increase was not observed.

The authors consider that their results are not in harmony with Nernst's views of the mechanism of solution, and certainly not in agreement with the assumption that no attraction exists between the solvent and the dissolving substance. Although they do not regard the existence of hydrates of alcohol as being definitely proved, the assumption that such hydrates are present would afford a logical explanation of their results. Other possible assumptions are that the dissolved substance forms condensed molecules in the mixtures of alcohol and water, or that the dissolved substance combines either with the alcohol or with the water.

H. C.

**Ternary Mixtures.** By WILDER D. BANCROFT (*Proc. Amer. Acad. Art. Sci.*, 1894, **30**, 324—368).—Since, in the application of the laws of gases to solutions, no difference has been observed between a solid and a liquid when dissolved, it appears probable that in all cases where a third substance,  $B$ , is added to a solution of  $A$  in  $S$ , the solubility of  $A$  undergoes a change. This variation may be large or small, positive or negative, depending on the nature of the three substances  $A$ ,  $B$ , and  $S$ . The author proposes the word "solute" for the substance dissolved in the liquid, and "consolute" liquids instead of infinitely miscible liquids.

The simplest case of a three-liquid system is when there are two practically non-miscible liquids, and a third with which each of the others is miscible in all proportions. Let  $A$  and  $B$  be two non-miscible liquids,  $S$  the common solvent with which  $A$  and  $B$  are miscible in all proportions when taken singly, and let the amount of  $S$  remain constant, so that we are considering the amounts of  $A$  and  $B$ , namely  $x$  and  $y$ , which will dissolve simultaneously in a fixed amount of  $S$ . This, being a case of equilibrium, must come under the general equation of equilibrium,

$$\frac{\partial F(x, y)}{\partial x} dx + \frac{\partial F(x, y)}{\partial y} dy = 0,$$

where  $dx$  and  $dy$  denote the changes in the concentrations of  $A$  and  $B$  respectively. If it is assumed in accordance with the Mass law that the change in solubility is a function of the amounts of  $A$  and  $B$  already present,

$$\frac{\alpha dx}{x} + \frac{\beta dy}{y} = 0,$$

or

$$\alpha d \log x + \beta d \log y = 0,$$

where  $\alpha$  and  $\beta$  are proportionality factors. If these are constants, and  $\alpha/\beta = n$ , we get, after integration and clearing of logarithms,

$$x^ny = \text{const.}$$

This is the expression representing the saturated solutions of two immiscible liquids in a constant quantity of a consolute liquid, and has been tested by the author and found to hold in cases where the pairs of immiscible liquids were chloroform and water, and benzene and water, and the consolute liquids methylic and ethylic alcohols and acetone, with the one exception of the chloroform-water-acetone series, where the disturbing effect is probably due to chloroform and acetone in presence of each other. It is found, however, that in most cases the concentrations cannot be given by one curve, but involve two, so that for one set of concentrations we have the relation  $x^ny = C_1$ , and for the other set  $x^ny = C_2$ . The two sets of saturated solutions correspond with different conditions. Thus, in the chloroform-water-alcohol series, the one set of solutions is saturated in respect to chloroform and not in respect to water; the other set is saturated in respect to water and not in respect to chloroform.

Analogous reasoning to the above is applied in the case in which we have two partially miscible liquids, and a third miscible in all proportions with each of the others. If  $s_1$  is the solubility of the first in the second, and  $s_2$  the solubility of the second in the first,

$$(x - s_2y)^n(y - s_1x) = \text{const.}$$

This relationship is tested in cases in which the partially miscible liquids are ether and water, and ethylic acetate and water, and the consolute liquids as before methylic and ethylic alcohols and acetone. When the liquids  $A$  and  $B$  are partially miscible, we have four curves instead of two. These refer to four distinct sets of equilibrium, there being the following four series of saturated solutions.

1. The solution is saturated in respect to  $B$ . Excess of  $A$  produces no precipitate.

2. The solution is saturated in respect to  $B$ . Excess of  $A$  or  $B$  produces a precipitate of  $B$ .

3. The solution is saturated in respect to  $A$ . Excess of  $A$  or  $B$  produces a precipitate of  $A$ .

4. The solution is saturated in respect to  $A$ . Excess of  $B$  produces no precipitate.

In addition to his own experiments, the author quotes those of others, more particularly of Pfeiffer (Abstr., 1892, 1046), in support of the above deductions. H. C.

**Equilibrium between Liquid and Solid Phases.** By H. W. BAKHUIS ROOZEBOOM and FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1894, 15, 588—638; compare Abstr., 1894, ii, 9).—The system considered is that of water, hydrochloric acid, and ferric chloride. The complete solubility isothermals for  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ ,  $+ 7\text{H}_2\text{O}$ ,  $+ 5\text{H}_2\text{O}$ ,  $+ 4\text{H}_2\text{O}$ , and anhydrous, were determined for varying hydrochloric acid contents. The curves are mapped against two axes representing the number of molecules of the acid and of ferric chloride per 100 mols. of water, and, as expected, are concave

to the former axis. The fields of equilibrium of the solution in presence of the phases  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  are hence determined, and from their intersection the line of equilibrium of the solution in the presence of two phases, and also the transition temperature from the state  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  to  $\text{Fe}_2\text{Cl}_6 + 7\text{H}_2\text{O}$ , &c., at varying percentage of hydrogen chloride. One ternary compound had been previously known,  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ . The author obtains two more. The first, represented by  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$ , is obtained as greenish crystals melting at  $-3^\circ$ ; the second,  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ , in the form of yellow crystals melting at  $-6^\circ$ . The solubility isothermals of these were mapped, and are the first examples of the complete realisation of such curves, being, as theoretically expected, closed curves. From their intersection with the isothermals previously obtained, the equilibrium conditions of the ternary phases, and of the combination of ternary and binary, are obtained. The effects of pressure are considered, and numerous experiments are recorded on the transition temperatures of the different compounds.

L. M. J.

**Influence of the Substitution of Halogens in Acids on the Rate of Etherification.** By D. M. LIGHTY (*Amer. Chem. J.*, 1895, **17**, 27—31).—The author has compared the etherification values of acetic, mono-, di-, and tri-chloroacetic and monobromoacetic acids at  $154^\circ$ . The values were determined at the end of 1, 2, 4, 6, 8, 10, 12, and 54 hours. No satisfactory results were obtained with trichloroacetic acid as it underwent secondary reactions, with evolution of gas which caused explosion of the tubes. One successful determination only was obtained, and even with that it is not improbable that the hydrogen chloride liberated influenced the result and made it untrustworthy. The initial rate of etherification increased with the addition of the halogen, and the limit with the mono- and di-chloro- and monobromoacetic acids was reached within half an hour.

	Initial rate.	Limit of etherification.
Acetic acid .....	46.95 per cent.	66.57 per cent.
Monochloroacetic acid..	67.01 „	66.62 „
Dichloroacetic „ ..	70.16 „	70.65 „
Trichloroacetic „ ..	—	93—94 (?) „
Monobromoacetic „ ..	65.87 „	65.87 „

With monobromoacetic acid, the amount of etherification diminished steadily after the first half hour, and was 43.46 per cent. at the end of eight hours. With monochloroacetic acid there was a similar reduction after 12 hours, reaching 46.93 per cent. after 54 hours. These results were undoubtedly due to secondary decomposition, but the character of the latter has not been yet ascertained.

L. T. T.

**Effect of Hydrolysis on Reaction Velocities.** By FREDERICK L. KORTRIGHT (*Amer. Chem. J.*, 1895, **17**, 116—122).—The term hydrolysis is employed to denote the decomposition of a salt in aqueous solution into a base and an acid by the action of the water. When any substance taking part in a reaction is hydrolysed, the total amount of the substance used cannot be taken as its *active*

mass; only the non-hydrolysed portion can be so considered. This is the case in the reaction studied by Kahlenberg (Abstr., 1894, ii, 346) between ferric chloride and stannous chloride. He has calculated his results on the assumption that the active mass of the reacting substances is the total amount taken, whilst in reality, since ferric chloride and stannous chloride are strongly hydrolysed, the active mass is much less.

The formula applying to this case,  $\frac{dx}{dt} = c(a - x)^2$ , on integration, yields

$$x/t(a - x) = ac = \text{const.}$$

Since tin and iron are nearly equally strong bases, we may assume that they are equally affected by the water, and since the experiments were carried out, using molecular proportions of each salt, we may assume that the relation continues molecular, and by plotting  $x = \phi(t)$  we can select a point where the curve becomes nearly parallel to the  $t$  axis, and  $(a - x) = h$  is approximately the amount of hydrolysed substance at that time. Assuming that the hydrolysis is constant throughout the experiment, the active mass at the beginning of the experiment becomes  $(a - h) = a'$ , and substituting this value for the initial active mass

$$x/t(a' - x) = a'c = \text{const.}$$

The author shows that  $a'c$  calculated by this means is more nearly constant than  $ac$ , the variations being such as would be produced by experimental error. H. C.

**Isomorphism.** By JAN W. RETGERS (*Zeit. physikal. Chem.*, 1894, 15, 529—587; compare Abstr., 1891, 146, 1151; 1892, 1048; 1893, ii, 193; 1894, ii, 85, 348).—The author in this communication considers the question whether isomorphous compounds can unite chemically, and regards the negative as the true answer. A list is given of the recorded exceptions, namely, double salts of isomorphous components, 15 in number, chiefly potassium-ammonium, sodium-lithium, sodium-silver, and calcium-barium compounds. These compounds are considered separately, and in every case, except that of barytocalcite, evidence is adduced to prove that the supposed double salt is merely a special case of an isomorphous mixture. The case for barytocalcite is not so clear, the evidence being conflicting and insufficient, and the author considers it requires further research. Experiments are then recorded, undertaken to see whether any double salts are obtainable amongst the vitriol series, solutions of two salts being mixed in different proportions, and the crystals obtained analysed. These experiments include observations on mixtures of the sulphates of iron and cobalt, zinc and magnesium, magnesium and nickel, iron and magnesium, iron and zinc, iron and copper, zinc and copper, and magnesium and copper. In no case is there any indication of the formation of a double compound, the composition of the mixed crystals varying continuously between the



end limits. The paper concludes with a controversial reply to the points raised by Rinne (*Zeit. physikal. Chem.*, **14**, 522).

L. M. J.

**Certain Regularities in the Weights of Drops of Molten Metals.** By KONSTANTIN THADDÉEFF (*Ber.*, 1895, **28**, 195—202).—If the end of a rod of metal is melted with a Bunsen burner or in the blow-pipe, and the falling drops collected and weighed, they will be found in the case of any one metal to have approximately the same weight. In the case of different metals, the weight of one drop multiplied by the atomic weight of the metal is also nearly the same in many cases. The following table of results may be quoted, the first set of experiments being made with the middle portion and the second set with the upper portion of one and the same rod of 7 mm. diameter in each case.

	Middle portion.			Upper portion.		
	No. of drops.	Weight of 1 drop.	Wt. of drop $\times$ at. wt.	No. of drops.	Weight of 1 drop.	Wt. of drop $\times$ at. wt.
Zinc.....	5	2.2071	143.4	5	2.1065	136.9
Lead.....	20	0.7664	158.6	23	0.8029	166.2
Tin.....	9	1.3172	155.4	10	1.1954	141.0
Bismuth.....	17	0.7266	152.6	30	0.5402	113.4
Cadmium.....	10	1.2378	138.6	9	1.2702	142.2
Antimony.....	12	0.5112	61.3	20	0.4954	59.4

Probably the product should be formed from the molecular rather than the atomic weight, for Quincke has already found that the weights of drops of similar salts give a constant when multiplied by the molecular weight. This may explain the discrepancy in the case of antimony. The volumes of the drops of lead and bismuth on the one hand and of tin and cadmium on the other are found to be the same.

H. C.

**Lamp for the Production of Formaldehyde.** By BERNHARD TOLLENS (*Ber.*, 1895, **28**, 261—263).—The production of formaldehyde by the incomplete combustion of methylic alcohol can readily be shown as a lecture experiment if an ordinary spirit lamp be used, and the wick, which should only project very slightly, be surrounded by a cage of fine platinum wire, which should be cylindrical in shape, with a rounded top, and about 2 cm. high by 1 cm. in diameter. A light is first applied, the flame then extinguished for a moment by putting on the glass extinguisher of the lamp, and then the extinguisher removed. The platinum cage remains red hot, and if it be protected from draughts by the tin chimney of an ordinary Bunsen burner, it will continue to glow for hours, large quantities of formaldehyde vapour being produced. The presence of the aldehyde may be recognised by the characteristic odour, or by collecting a little of the vapour in a moistened inverted beaker and adding ammoniacal silver oxide or magenta decolorised by sulphurous acid. Another

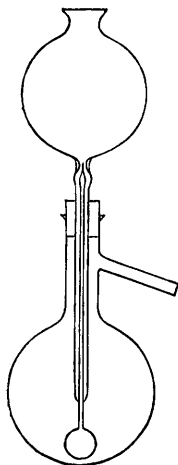
method of exhibiting the presence of the aldehyde is to collect the vapour in an inverted beaker moistened with ammonia solution, and then add a little water and bromine water. A thick precipitate of hexamethylenamine tetrabromide is at once produced.

The author suggests that the lamp may be of use for the production of a disinfecting atmosphere, since formaldehyde is preferable to chlorine or sulphurous anhydride in many cases. A. H.

**A New Laboratory Barometer.** By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1894, [3], **11**, 447—448).—A portable syphon barometer, arranged to give corrected values of pressure with two readings and one addition or subtraction. The diameter of the reservoir is considerably greater than that of the tube; the latter alone is graduated, and the graduations are arranged to allow for the change of level in the reservoir, so that the corrected height is given by a single reading. The temperature correction is given by an attached thermometer, graduated to show the various values of  $750(\alpha - K)t$ , where  $750$  = mean barometer height in mm.,  $K$  and  $\alpha$  = coefficient of expansion of glass and mercury,  $t$  = temperature. The neglect of the variation of this temperature correction with the height of the barometer involves a maximum error of only 0.1 mm. The instrument is therefore available for all ordinary purposes. JN. W.

**Substitute for a Funnel in Filtering.** By ARTHUR M. EDWARDS (*Chem. News*, 1895, **71**, 40).—A perforated piece of celluloid, bent to the shape of a funnel, is used by the author for supporting the filter-paper. D. A. L.

**Simple Substitute for a Separator Funnel.** By D. HOLDE (*Zeit. anal. Chem.*, 1895, **34**, 54).—An ordinary bottle or flask is fitted with a cork, through which pass two tubes. One of these, terminating inside level with the cork, is furnished with a stop-cock or pinch-clamp. The other, reaching to the bottom of the vessel, is there narrowed to a point, and serves to admit air. After shaking, the vessel is inverted for drawing off the two layers separately. M. J. S.



**Constant-level Apparatus.** By JOHN C. CHORLEY (*Analyst*, 1895, **20**, 16).—The small bulb at the end of the long, thin tube (see illustration) floats on the surface of the liquid. Its ground upper end fits into the thickened part of the larger tube, and prevents the liquid contained in the large bulb from flowing into the flask. When, however, the level of the liquid falls, the upper end of the long tube drops away and releases a small quantity of the liquid, so that the level is automatically maintained during the distillation. L. DE K.

**Sodium Press as Modified by E. Beckmann.** By REINIGER, GEBBERT, and SCHALL (*Ber.*, 1895, 28, 322—324).—The principal improvements are two. The screw and plunger are made of separate pieces of metal, and joined in such a manner that when the former is rotated the latter moves vertically. The lower part of the cylinder is removable without interference with the rest of the press, so that various shaped nozzles may be used to give wire or ribbon, as desired.  
J. B. T.

**Two New Laboratory Apparatus.** By HANS LOESNER (*J. pr. Chem.*, 1894, [2], 50, 561—562).—A stirring apparatus and a water bath are figured. The former consists of a perforated porcelain or metal cylindrical shell, vertically disposed, and having for its axis a rod which is capable of rapid rotation by a small water turbine attached to the same retort stand. The water bath is of a common pattern, but is fitted with an iris diaphragm in place of the usual rings.  
A. G. B.

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## Inorganic Chemistry.

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**Combination of Sulphur with Iodine.** By C. E. LINEBARGER (*Amer. Chem. J.*, 1895, **17**, 33—59).—By mixing solutions of iodine and of sulphur in carbon bisulphide, and allowing the mixtures to evaporate, the only compound of sulphur and iodine obtained had the formula  $S_nI_n$ ; it crystallised in black, rhombic tablets, melting at  $66.1-66.2^\circ$ . The same compound was obtained by the action of sulphur chloride ( $S_2Cl_2$ ) on ethylic iodide, on propylic iodide, and on amylic iodide. Determinations of the variation of melting point of different mixtures of sulphur and iodine gave a curve indicating the formation of only one compound, of the formula  $S_nI_n$ . From analogy with the chloride and bromide, it is probable that the formula is  $S_2I_2$ , and this is confirmed by the influence exerted by the compound (and also by varying mixtures of sulphur and iodine) on the boiling point of carbon bisulphide. Whilst these results do not exclude the possibility of the existence of other compounds of sulphur and iodine, no indication of their formation could be obtained. The compound  $S_2I_2$  itself is in a very feeble state of combination, and sulphur and iodine atoms seem to have more tendency to form molecular aggregations than to combine with each other.

Full details and curves of results are given, and also a historical survey of previous work on the subject. L. T. T.

**Preparation of Nitric Oxide.** By MASUMI CHIKASHIGÉ (*Chem. News*, 1895, **71**, 16—17).—Contrary to the experience of Johnstone (Abstr., 1882, 692), the author finds that when potassium thiocyanate and cobalt nitrate are heated together, whether dissolved or not, no

evolution of nitric oxide takes place; but in the latter case, by continuing the heating after evaporating to dryness, a violent action soon sets in, with copious disengagement of gas, consisting (to the extent of about two-thirds) of nitric oxide, mixed chiefly with nitrogen; carbonic anhydride and ammonia are likewise produced. The residue is then ammoniacal and black, owing to the presence of cobalt sulphide, but, unlike Johnstone's residue, it does not contain free sulphur or carbon. The action of dilute nitric acid on potassium thiocyanate is, however, not affected by the presence of cobalt nitrate. Possibly Johnstone's cobalt nitrate solution contained free nitric acid.

D. A. L.

**Action of Metals on Nitric acid.** By GEORGE O. HIGLEY (*Amer. Chem. J.*, 1895, 17, 18—27).—This is a continuation of the work of Freer and Higley (*Abstr.*, 1893, ii, 273). Acids of different strengths were employed, the acid being always in large excess. The metals experimented with were copper and lead. No successful results could be obtained with lead on using acid of sp. gr. above 1.35, as the insolubility of lead nitrate in strong nitric acid caused the formation of a protective coating of salt over the metal. The author draws the following conclusions. 1. Nitric acid of sp. gr. 1.30, or more, when reduced by copper, yields only nitrous anhydride and nitric peroxide, the former increasing and the latter diminishing rapidly with increasing dilution of the acid. 2. Nitric oxide is a product of decomposition of nitrous anhydride and nitric peroxide, when the sp. gr. of the acid is 1.25 or more; and of nitrous anhydride alone when the gravity of the acid is below 1.25. 3. Lead reacts much more readily than copper, producing with equal concentration of acid relatively much more nitrous oxide, and less of the higher oxides of nitrogen. 4. The remarkable difference in the composition of the products of reduction favours the theory of direct deoxidation rather than that it is due to nascent hydrogen.

L. T. T.

**Volatilisation of Carbon.** By HENRI MOISSAN (*Compt. rend.*, 1894, 119, 776—781).—When a carbon tube of about 1 cm. diameter is heated in an electric furnace with an arc produced by a current of 2,000 ampères and 80 volts, a light black cloud forms in the interior, in consequence of the condensation of carbon vapour. If a dish containing crystallised silicon is placed in the tube, the silicon melts and then boils, and its vapour, coming into contact with the vapour of the carbon, forms slender needles of carbon silicide. No evidence of the fusion of carbon can be obtained, even with a current of 2,200 ampères and 70 to 80 volts, although the temperature is sufficiently high to rapidly volatilise calcium and magnesium oxides. With powerful currents like these, it would seem that with a small furnace the temperature increases with the intensity of the current, although probably with weaker currents the temperature is to some extent limited by the volatilisation of the carbon.

In all cases, the carbon subjected to these high temperatures is converted into graphite. The black deposit formed on the internal surface of incandescent lamps consists of amorphous graphite

mixed with crystals of carbon silicide and some other crystals that seem to be silica.

The carbon vapour, whether condensed in a carbon tube, or on the exterior of a copper tube kept cool by internal circulation of water, or on the electrodes themselves, condenses always in the form of graphite, and the deposits show no traces of fusion.

When the filament of an incandescent lamp breaks, the fractured ends show no traces of fusion, but are covered with small crystals of graphite.

It follows that carbon, like arsenic, volatilises under ordinary pressure without previously fusing. It is probable, however, that under a sufficiently high pressure fusion would take place. The diamonds obtained by the author in ingots of iron cooled in lead have the appearance of elongated drops, and Brazilian and Cape diamonds are found without any apparent crystalline form, but with the rounded forms assumed by a liquid kept in fusion in the interior of a pasty mass.

C. H. B.

**Double Chlorides and Bromides of Cæsium, Rubidium, Potassium, and Ammonium with Ferric Iron. Two Ferroso-ferric Double Bromides.** By P. T. WALDEN (*Amer. J. Sci.*, 1894, [3], 48, 283—290).—The following ferric salts were obtained.

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
$\text{Cs}_3\text{FeCl}_6, \text{H}_2\text{O}$	$\text{Cs}_2\text{FeCl}_5, \text{H}_2\text{O}$	$\text{CsFeCl}_4, \frac{1}{2}\text{H}_2\text{O}$
—	$\text{Cs}_2\text{FeBr}_5, \text{H}_2\text{O}$	$\text{CsFeBr}_4$
—	$\text{Rb}_2\text{FeCl}_5, \text{H}_2\text{O}$	—
—	$\text{Rb}_2\text{FeBr}_5, \text{H}_2\text{O}$	—
—	$\text{K}_2\text{FeCl}_5, \text{H}_2\text{O}$	—
—	$(\text{NH}_4)_2\text{FeCl}_5, \text{H}_2\text{O}$	—
—	—	$\text{NH}_4\text{FeBr}_4, 2\text{H}_2\text{O}$ .

The compounds  $\text{K}_2\text{FeCl}_5, \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{FeCl}_5, \text{H}_2\text{O}$ , have been previously made by Fritzsche (*J. pr. Chem.*, 18, 483). The salt,  $\text{Rb}_2\text{FeCl}_5, \text{H}_2\text{O}$ , is probably Godeffroy's salt,  $\text{Rb}_3\text{FeCl}_6$ , as the author was unable to obtain any rubidium salt of this formula. The salt  $\text{CsFeCl}_4$  is so very hygroscopic that it is very difficult to analyse, and it is possible that it is really an anhydrous salt, and that the  $\frac{1}{2}\text{H}_2\text{O}$  found was hygroscopic moisture.

Two unstable, dark green compounds,  $\text{RbBr}_2\text{FeBr}_2, 2\text{FeBr}_3, 3\text{H}_2\text{O}$  and  $\text{KBr}_2\text{FeBr}_2, 2\text{FeBr}_3, 3\text{H}_2\text{O}$ , were also prepared, but no similar compounds could be obtained with the other alkali or ammonium haloids. The crystals of the rubidium salt are rhombohedral, those of the potassium salt cubical.

L. T. T.

**Cæsium-Cobalt and Cæsium-Nickel Double Haloids.** By G. F. CAMPBELL (*Amer. J. Sci.*, 1894, [3], 48, 418—420, and *Zeit. anorg. Chem.*, 8, 126).—The following salts were obtained.

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
$\text{Cs}_3\text{CoCl}_5$	$\text{Cs}_2\text{CoCl}_4$	$\text{CsCoCl}_3, 2\text{H}_2\text{O}$ .
$\text{Cs}_3\text{CoBr}_5$	$\text{Cs}_2\text{CoBr}_4$	—
—	$\text{Cs}_2\text{CoI}_4$	—
—	—	$\text{CsNiCl}_3$
—	—	$\text{CsNiBr}_3$ .

These results show that cobalt forms double salts more readily than does nickel, and also confirms the previously observed increase in ease of formation of double salts from the iodides to the chlorides.

The colour of the chlorides containing cobalt is a magnificent blue, the bromides and iodides containing the same metal are green, and the two nickel salts yellow. All the salts are crystalline, and whiten, from decomposition, when brought in contact with water or alcohol.

L. T. T.

**Solutions of Metallic Silver.** By M. CAREY LEA (*Amer. J. Sci.*, 1894, [3], 48, 343).—The solutions of metallic silver previously described by the author (*Abstr.*, 1892, 15, and 116) are colloidal, and will not pass through membranes. They are perfect solutions showing no turbidity, even when viewed under a top light so that the incident ray makes a right angle with the line of view. This disproves the contention of Barus and Schneider that in them the silver is not allotropic, but is ordinary silver in a very fine state of division. When carefully made, they are very permanent; one, kept exposed to daylight for three years, still contained much dissolved silver, although part of the silver was deposited in a white metallic form where the light was strongest.

L. T. T.

**Action of Dry Hydrogen Chloride on Serpentine.** By EDWARD A. SCHNEIDER (*Zeit. anorg. Chem.*, 1894, 8, 98—102). An answer to R. Brauns (*Abstr.*, 1894, ii, 284).—From the analytical data given in the original paper, the author concludes that (1) water is formed by the action of dry hydrogen chloride on serpentine; (2) a portion of this water is carried away by the hydrogen chloride, the remainder being retained by the silicate residue; (3) the silicate residue, when treated with dry hydrogen chloride, behaves in the same manner as the original serpentine, and water and magnesium chloride are formed; part of the water is retained by the silicate residue.

E. C. R.

**Atomic Weight of Thallium.** By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1894, [3], 11, 423—424).—The mean of the author's results calculated by Clarke (*J. Amer. Chem. Soc.*, 16, No. 3), namely, 203.57, is too low, owing to the inclusion of a number misprinted in the original paper. The true mean is 203.62. The author raises the question: to what point is it justifiable to maintain the immutability of the atomic weights?

JN. W.

**The Molecular State of Mercurous Chloride Vapour.** By VICTOR MEYER (*Ber.*, 1895, 28, 364—366; compare this vol., ii, 46).—

In reply to the renewed criticism of Fileti (*J. pr. Chem.*, [2], 51, 197), the author again points out that his experiments show that Fileti's gold amalgamation test does not succeed even with a mixture known to contain the vapours of mercury and mercuric chloride. The extent of dissociation of the mercurous chloride vapour would only be diminished by the introduction of an excess of mercuric chloride vapour if the dissociation were incomplete, not when, as is really the case, it is complete (compare Horstmann, *Annalen*, Suppl. 6, 74). The author's experiments throw no light on the molecular formula of mercurous chloride.

A. H.

**Action of Aluminium on Carbon and its Compounds.** By LÉON FRANCK (*Bull. Soc. Chim.*, 1894, [3], 11, 439—446).—Mallet has shown (*Trans.*, 1876, 349) that carbonic oxide is reduced to carbon by aluminium. The action on carbonic anhydride is similar, as, when aluminium powder is heated to redness in a stream of that gas, the latter is reduced to carbon.

The alkali carbonates are reduced to metal when heated with aluminium in the proportion  $M_2CO_3 : 2Al$ . The yield of lithium and potassium is good, and, as the carbonic oxide compound is not formed in the latter case, the process promises to become of commercial importance. The reaction with sodium carbonate proceeds best in an atmosphere of hydrogen.

*Aluminium carbide* is formed by heating aluminium powder with lamp-black; it yields acetylene in abundance when treated with dilute hydrochloric acid. The author has not yet succeeded in separating it from unchanged lamp-black.

JN. W.

**Atomic Weight of Nickel and Cobalt.** By CLEMENS WINKLER (*Zeit. anorg. Chem.*, 1894, 8, 1—11).—The method of determining the atomic weights of nickel and cobalt by treating the pure metal with an excess of sodium aurochloride, or potassium aurochloride is not accurate, because the precipitated gold always contains small quantities of nickel or cobalt. The results obtained by warming the metal with hydrochloric acid containing platinic chloride, passing the hydrogen evolved over glowing copper oxide, and weighing the water formed, are not satisfactory. The numbers obtained varied, in the case of nickel, from 58.9494 to 59.2241, and in the case of cobalt from 59.0161 to 59.3487.

The method which the author finds most satisfactory, is to deposit the metal by the electric current on a platinum electrode, dissolve it in an excess of iodine in potassium iodide, and then estimate the excess of iodine by sodium thiosulphate.

The iodine employed was purified by mixing it with 10 per cent. of its weight of freshly-heated potassium iodide, allowing the mixture to remain for some weeks in thin layers over sulphuric acid, and then subliming the iodine into a perfectly dry, stoppered bottle. One part by weight of the metal is treated with 5 parts of the pure iodine, and with the same quantity of potassium iodide in the form of a 40 per cent. solution, and the mixture is allowed to remain one day in a tightly stoppered vessel. The excess of iodine is estimated by



means of a solution of sodium thiosulphate, of which 1 c.c. = 0.012645 gram of iodine.

The pure nickel is prepared as follows. 32.84 grams of the purest nickel sulphate is dissolved in 1 litre of water. 200 c.c. of this solution is mixed with 30 grams of ammonium sulphate, 50 grams of ammonia (sp. gr. = 0.905), and 250 c.c. of water, and the nickel deposited on a highly polished nickel cathode, the anode being of platinum. A current of 2.8 volts and 0.8 ampère is employed, the current density being 0.5 ampère per 100 sq. cm. The current is continued until the deposited nickel separates from the cathode in thin plates. The metal is then heated in a current of dry hydrogen. No alteration in weight was observed after heating in hydrogen, showing that the metal was quite free from oxides.

The pure cobalt is prepared in a similar way. The electrolyte consists of 100 c.c. of a solution of cobalt sulphate containing 11.64 grams of cobalt per litre, 30 grams of ammonium sulphate, 30 grams of ammonia, and 500 c.c. of water. A platinum cathode and anode were employed. A current of 3.0 volts and 0.7 ampère is employed, the current density being 0.6 ampère per 100 sq. cm. The metal thus obtained is contaminated with a small quantity of oxide, which is reduced by heating it in a current of hydrogen. Two preparations contained 0.32 and 0.21 per cent. of the cobalt as oxide respectively.

The mean results obtained from the first series of five experiments were (1) Ni = 58.6878, Co = 59.3849; from the second series of three experiments, (2) Ni = 58.7433, Co = 59.3507. This gives, as the mean of all the observations, Ni = 58.7155, Co = 59.3678, taking H = 1 and I = 126.53.

E. C. R.

**Action of Reducing Agents on Potassium Nickelocyanide and Magnetic Oxide of Nickel.** By THOMAS MOORE (*Chem. News*, 1895, 71, 81—82).—Continuing his experiments, the author finds that the red compound (Abstr., 1894, i, 102) may also be obtained from potassium nickelocyanide by the action of zinc coated with silver or copper, or by the electrolysis of the solution in the presence of excess of alkali with a mercury cathode; potassium cyanide is set free. By adding nickel sulphate to convert this into the double cyanide, and by continuing the electrolysis, a more concentrated red solution may be obtained, but ultimately the mercury commences to swell up, in a manner similar to ammonium amalgam, and minute mercury globules float in the solution; the precipitate which the red solution gives with hydrochloric acid is decomposed on drying, and the isolation of the cyanide has not been accomplished. The oxide, however, has been obtained by boiling the solution with ammonium chloride in a non-oxidising atmosphere, washing the precipitate free from cyanide, &c., by decantation, first with hot water, then with boiling dilute ammonia containing a little ammonium chloride, and finally with distilled water. When dried at 100°, it is a heavy, black mass, strongly magnetic, not attacked by carbonic oxide, and apparently not altered by exposure to the air at the ordinary temperature; it is soluble in sulphuric acid with evolution of hydrogen, and in nitric acid with evolution of red fumes, green nickel salts

being formed in both cases. Potassium cyanide dissolves it with evolution of hydrogen, and, if in a non-oxidising atmosphere, with partial reproduction of the red cyanide. It is decomposed by silver nitrate with the separation of metallic silver. Although it has not been obtained in a state of purity, numerous analyses point to a hydrated nickel suboxide,  $\text{Ni}_3\text{O}_2 \cdot \text{H}_2\text{O}$ , a composition foreshadowed by the results of previous experiments (*loc. cit.*). D. A. L.

**Titanium.** By EDWARD A. SCHNEIDER (*Zeit. anorg. Chem.*, 1894, 8, 81—97).—The product obtained by reducing potassium titanofluoride with sodium in an atmosphere of pure hydrogen is not pure titanium. It gave, on analysis, insoluble residue ( $\text{TiCu}$  and  $\text{TiO}_2$ ) = 4.53 per cent.,  $\text{H}_2\text{O}$  = 0.74,  $\text{Ti}$  = 84.88,  $\text{Cu}$  = 2.52,  $\text{Fe}$  = 0.18,  $\text{O}$  = 6.36,  $\text{KF}$ ,  $\text{NaF}$  and  $\text{H}$  by difference = 0.79 per cent. Disregarding the other impurities, these numbers give  $\text{Ti}$  = 75.34 per cent.,  $\text{TiO}_2$  = 15.90 per cent. This impure amorphous titanium absorbs hydrogen with avidity, and takes fire on exposure to air, with the formation of water and titanous acid. Titanium which has been in contact with water for some time does not take fire spontaneously on exposure to air, but, on heating, it burns, with the production of the hydrogen flame. The author was unable to determine whether a titanium hydroxide or hydride is formed. 0.0986 gram of titanium when treated with hydrochloric acid, gave 65.37 c.c. of hydrogen, whereas, according to the equation  $\text{Ti} + 3\text{HCl} = \text{TiCl}_3 + 3\text{H}$ , only 60.52 c.c. hydrogen should have been produced. The impure amorphous titanium, when thoroughly washed with water, does not decompose water at  $100^\circ$ . When heated in the air at  $100$ — $120^\circ$  for 15 hours, it took up oxygen only to the extent of 0.06 per cent., and, after heating for 17 hours at  $150$ — $160^\circ$ , the oxygen absorbed only amounted to 0.48 per cent. It is scarcely attacked by dilute hydrochloric acid at the ordinary temperature, and the fuming acid acts only slowly at  $15^\circ$ . At temperatures up to the melting point of combustion tubing, titanium does not reduce either silica or alumina.

An alloy of titanium and copper is obtained by reducing potassium titanofluoride with sodium in the presence of copper at a bright red heat. It is hard and brittle, and contains 11.85 per cent. of titanium. If the reduction is conducted in a copper vessel, the latter becomes covered with a silver-white coating of the alloy, and is hard enough to withstand scratching with steel. If aluminium is melted with titanous oxide and copper under a protecting layer of sodium and potassium chlorides, an aluminium bronze is obtained, containing small quantities of titanium.

**Titanium nitride.**—The product obtained by heating titanium ammonio-chloride in a current of ammonia, according to the author's analysis, contains 5.4 per cent. of oxygen. When heated for half an hour at a red heat in a current of steam, 41.83 per cent. remains unchanged, and, when heated for an hour in dry hydrogen chloride, 67 per cent. remains unchanged. When heated at a white heat in a current of nitrogen, the indigo-blue nitride is converted into a brownish-yellow product and loses about 3.9 per cent. in weight. When titanium, prepared in the above manner, is heated at a red heat

in a stream of ammonia, the indigo-blue nitride is also obtained. In the hope of determining the relative affinity of nitrogen to titanium, boron and magnesium, the author heated titanium nitride with magnesium and boron, boron nitride with magnesium and titanium, and magnesium nitride with boron and titanium, but in neither case was any action observed.

A crystalline, greyish-black sulphide, probably titanium sesqui-sulphide, is obtained by heating the above blue nitride to redness and passing over it sulphur vapour by the aid of a current of hydrogen.

*Titanium tetrachloride cyanobromide*,  $\text{TiCl}_3 \cdot \text{N} : \text{CClBr}$ , is obtained by gently heating a mixture of cyanogen bromide and titanium tetrachloride. It crystallises in beautiful crystals, resembling in colour potassium aurochloride, and forms a cherry-red additive product with dry ammonia. When heated in ammonia, it yields the nitride and some cyanamide. When a mixture of cyanogen and nitrogen is led over titanium at a red heat, an amorphous, black compound is obtained, which, when heated in a current of dry chlorine, yields titanium tetrachloride cyanochloride, and titanium tetrachloride.

The author was unable to prepare titanochloroform. Dry hydrogen chloride forms with titanium at  $300^\circ$  a non-volatile compound containing chlorine. Probably titanochloroform is formed, together with titanium tetrachloride, at higher temperatures.

When a solution of titanous acid in sulphuric acid is mixed with an insufficient quantity of tartaric acid, and is then incompletely neutralised with ammonia, the titanous acid is precipitated quite free from admixture with iron. The titanous acid thus obtained becomes gelatinous by repeated treatment with water, then dissolves in a large quantity of water, and may be further purified by dialysis.

E. C. R.

**New Methods of obtaining Platinosochlorides, and Probable Existence of a Platinum Subchloride.** By M. CAREY LEA (*Amer. J. Sci.*, 1894, [3], 48, 397—401).—When potassium platinochloride (12 grams) is heated in a covered vessel, on a water bath, with hydrogen potassium sulphite (9 grams) and water (160 c.c.) for 10—12 hours, the reduction is complete, and the red salt crystallises out on evaporation. Similar results are obtained by heating the platinochloride (9 grams) with potassium hypophosphite (1 gram) and water (300 c.c.), at  $80$ — $90^\circ$ , for 18—20 hours. The completion of the action is shown by the pure ruby colour of the solution, the least shade of orange indicating the presence of platinochloride. The first method is the safest, as the reduction cannot go beyond the platinosochloride, but in the second method, the red salt separates more easily and completely, and, with care, very good results are obtained.

If, when reducing with potassium hypophosphite, the action is continued after complete conversion into the red salt, the solution rapidly changes to dark brown. Hydrochloric acid has no effect on this solution, nitric acid decolorises it, potash causes a brown precipitate soluble in excess of the precipitant, and ammonia a brown precipitate insoluble in excess. This compound could not be isolated, but is probably a subchloride.

L. T. T.

## Mineralogical Chemistry.

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**Dufrenoyite from the Binnenthal.** By HEINRICH BAUMHAUER (*Zeit. Kryst. Min.*, 1895, **24**, 85—87).—The author gives a crystallographical description of some specimens of dufrenoyite from the Binnenthal. The crystals, which were about 2 cm. long and 8 mm. broad, formed rounded prisms, and yielded, on analysis,

Pb.	As.	S.	Sp. gr.
57.42	20.89	22.55	5.52

B. H. B.

**Zinckenite from Oruro, in Bolivia.** By A. W. STELZNER (*Zeit. Kryst. Min.*, 1895, **24**, 125—127).—A description having been published of sundtite from Oruro (*Zeit. Kryst. Min.*, **24**, 124), the author gives an account of a specimen from the same locality in the museum of the Freiberg School of Mines. This, however, although very similar in appearance, is not sundtite, but an argentiferous zinckenite of the following formula,  $2\frac{1}{2}(\text{PbS}, \text{Sb}_2\text{S}_3) + (\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3)$ . B. H. B.

**Iron Nickel Pyrites from Norway.** By J. H. L. VOGT (*Zeit. Kryst. Min.*, 1895, **24**, 139).—This mineral, first described by Scheerer in 1845, has hitherto been found at but one locality, Espedalen, in Norway. It has, however, now been met with among some nickel ores from Eiterjord, on the southern side of the Beiern river. It is similar in all respects to Scheerer's mineral, except that the proportion of nickel is somewhat less, its analysis having yielded

Fe.	Ni.	Co.	S.	Cu.	Insoluble.	Total.
30.51	32.97	0.45	34.15	0.28	0.29	98.65

B. H. B.

**Free Alkaline Earths in Rocks containing Carbonates.** By A. LEMOINE (*Bied. Centr.*, 1894, **23**, 726—728; from *Jour. Assoc. anciens élèves Inst. Agric., Gembloux*, 1894, **4**, 275—280).—Raspail has stated that free calcium oxide occurs in some rocks containing carbonates. The lime cannot be detected by means of the usual indicators, since the carbonates dissolve sufficiently in boiling water to give an alkaline reaction. The following results of analyses of two rocks, (A) Russian limestone, (B) Belgian dolomite, point to the presence of free alkaline bases.

	Water.	Organic matter.	Combined water.	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .
A ....	0.174	0.295	—	0.813	0.075	0.162	0.052
B ....	0.244	1.610	2.190	0.656	0.602	0.063	—
		SO <sub>3</sub> .	CO <sub>2</sub> .	CaO.	MgO.		
A .....		0.002	43.003	55.098	0.370		
B .....		—	38.070	33.862	21.812		

Supposing the carbonic anhydride to be in combination with lime and what is over with magnesia, A will contain 0.370 per cent. of free lime and 0.370 per cent. of free magnesia, whilst B will contain 11.380 per cent. of free magnesia. The silica in A is present as quartz sand, and is not combined. When the powdered limestone is shaken with water, it at once shows an alkaline reaction.

As regards the presence of the free bases, it is supposed that waters containing the free bases and organic matter became mixed, giving rise to a precipitate consisting of the organic matter and alkaline earths. This decomposed with production of carbonates, any excess of bases over the carbonic anhydride produced remaining free. The density of the layers prevented the subsequent percolation of water containing carbonic anhydride.

If the author's theory is correct, it involves the formation of the strata in question in a shorter time than has hitherto been supposed. N. H. J. M.

**Kämmererite from Tampadel, in Silesia.** By K. KOSMANN (*Zeit. Kryst. Min.*, 1895, **24**, 198).—In the chrome iron ore deposit, near Tampadel, kämmererite, or rhodochrome, occurs with quartz and chlorite, in the form of violet to greenish, transparent, pyramidal crystals 5 to 6 mm. in length.

An analysis of magnochromite, from the same district, gave the following results.

Cr <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	SiO <sub>2</sub> .
40.25	19.90	1.48	13.46	16.79	7.80

together with traces of vanadium.

B. H. B.

**A New Arsenate from Laurium.** By L. MILCH (*Zeit. Kryst. Min.*, 1895, **24**, 100—103).—In a series of minerals from the Laurium mines, in Greece, a new mineral resembling scorodite was found. It occurs in the form of brownish-red, minute crystals, belonging to the rhombic system, and giving, on analysis, the following results.

As <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	PbO.	SiO <sub>2</sub> .	CaCO <sub>3</sub> .	H <sub>2</sub> O.	Total.
33.44	3.74	34.53	10.63	1.13	1.46	15.55	100.48

The formula is 2PbSO<sub>4</sub>.6As<sub>2</sub>O<sub>5</sub>(FeOH)<sub>3</sub> + 27H<sub>2</sub>O. For this new mineral the author suggests the name of *lossenite*, in memory of C. A. Lossen. B. H. B.

**Phenacite from Ober-Neusattel.** By CARL VRBA (*Zeit. Kryst. Min.*, 1895, **24**, 119—123).—At Ober-Neusattel, near Pisek, in Bohemia, the author has found in the felspar and quartz several cavities lined with phenacite and albite. Crystallographically, the phenacite resembles that of Reckingen, in Switzerland, and that of Mt. Antero, in Colorado. Analysis yielded the following results.

SiO <sub>2</sub> .	BeO.	H <sub>2</sub> O.	Total.	Sp. gr.
54.27	45.17	0.53	99.97	2.963

B. H. B.



## Physiological Chemistry.

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**Effect of Calcium Phosphate and Carbonate on Increase of Live Weight.** By J. NEUMANN (*Bied. Centr.*, 1895, **24**, 34—35; from *Jour. f. Landw.*, **42**, 33).—In the author's experiments on the assimilation of lime and phosphoric acid mixed with food (*Bied. Centr.*, 1894, **23**, 588), the effect of the minerals on the live weight was kept in view. In the two experiments now described, the calves were fed with milk alone, and with milk to which calcium phosphate and carbonate, respectively, were added. The effect of minerals was to increase the change of substance, and hence to diminish the increase in live weight.

The urine of the calves was in each case free from sugar, although 11 grams of milk sugar per kilo. of live weight was given. Stohmann found sugar in the urine of bullocks which had had only 4 grams of sugar per kilo. The nitrogen of the urine was mostly in the form of urea.

N. H. J. M.

**Action of Intravenous Injection of Sodium Chloride on the Composition of Blood and Lymph.** By WILHELM COHNSTEIN (*Pflüger's Archiv*, 1895, **59**, 508—524).—In previous communications, the author advanced certain experiments which tell against Heidenhain's theory that lymph formation is due to a process analogous to secretion by the endothelial cells of the walls of the blood-vessels, and Starling (*Abstr.*, 1894, ii, 424) has also made similar observations. The present experiments with injections of sodium chloride support the previous contention that the alterations in blood and lymph are the consequences of physical processes, especially diffusion and filtration. Any theory of secretory activity is regarded as superfluous.

W. D. H.

**Ferratin and Iron in the Liver.** By FRANZ VAY (*Zeit. physiol. Chem.*, 1895, **20**, 377—402).—Iron in the liver, as a result of the destruction of red blood corpuscles, has been the subject of numerous investigations by microchemical and other methods. Full references are given. Zaleski has described a definite compound to which he

has given the name hepatin. Bunge, in egg-yolk, has found an iron compound with nucleo-albumin; and Schmiedeberg (this vol., i, 196) gave the name ferrialbuminic acid or ferratin to a compound in the liver which is coloured black by ammonium sulphide. His method did not lead to the isolation of iron compounds of nuclein from the liver. The present research relates chiefly to the estimation of ferratin in the liver in health and disease. The average in the liver of the lower animals gives a percentage of 0.15—0.3 of ferratin (iron 0.01—0.018 per cent), but the human liver contains less. It runs parallel with the condition of nutrition. In siderosis, of which five cases were examined, there was only one in which the amount of ferratin was increased markedly.

W. D. H.

**Red Pigment of "*Diemyctylus viridescens*."** By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1894, **119**, 912—913).—The skins of the small lizard, *Diemyctylus viridescens*, were exhausted with boiling alcohol and ether, and, after evaporating the solvents, the residue was treated with sodium hydroxide solution and the pigment extracted with benzene. It has the composition C, 60.27; H, 4.52; N, 7.16, which agrees well with the formula  $C_{20}H_{18}N_2O_7$ . It shows no characteristic absorption bands. It dissolves in alcohol, ether, benzene, and carbon bisulphide, but is insoluble in water, acids, and alkalis. When boiled for a long time with hydrochloric acid, the pigment, which the author calls *diemyctylin*, is converted into uric acid, hence it would seem that it is an excretory product deposited under the epidermis.

C. H. B.

**Action of Dilute Alkalis on Lower Animals and Plants.** By THOMAS BOKORNY (*Pflüger's Archiv*, 1895, **59**, 557—562).—Previous work by the author has shown that certain dilute alkaline substances do not kill some of the lower plants, but cause a change in the cytoplasm which is best designated by Darwin's term "aggregation." The present research deals chiefly with some of the low forms of animal life.

Caffeine (1 per 1000) does not kill amœbæ, but it causes vacuolation, and increase in the refractive index of the protoplasm—a change very similar to that noted in plant cells; in paramœcium, the change is very similar. Ammonia (which is much more fatal), ammonium carbonate, and potassium hydroxide produce analogous results.

W. D. H.

**Rotatory Action of Lactates.** By FELIX HOPPE-SEYLER and TRASABURO ARAKI (*Zeit. physiol. Chem.*, 1895, **20**, 365—376).—The paralactates of zinc, calcium, and lithium rotate the plane of polarised light differently in solutions of different degrees of concentration; so that the value  $[\alpha]_D$  rises with the dilution of the solution. For equal weights of lactic acid, this value is lowest for calcium and highest for lithium lactate. The lithium salts, on account of their ready solubility, the ease in drying them, and their good crystallisation and relatively high specific rotation, serve well for the estimation of lactic acid by circular polarisation.

The solutions of optically active lactates from rabbit's urine, obtained by lessening the oxygen supply, or by poisoning with car-



bonic oxide, give values corresponding very well with those of paralactates of the same concentration obtained from meat extract.

In the urine of rabbits which have been subjected for some time to carbonic oxide poisoning, there is found, after subcutaneous injection of an aqueous solution of sodium fermentation lactate, a mixture of optically inactive lactic acid and dextrorotatory lactic acid. The optically active acid indicates a change, in the organism, of part of the lactate given into paralactate.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effect of Chlorides on the Growth of Plants.** By WYPFEL (*Bied. Centr.*, 1894, **23**, 853; from *Bot. Centr.*, 1893, **55**, 182).—The chlorides of magnesium, calcium, potassium, and ammonium, in which the bases are of importance to vegetation, act at first favourably, but afterwards unfavourably on plants, as they become too concentrated, and even destroy the plants. Magnesium chloride was generally the least injurious, potassium and ammonium chlorides the most injurious; 0.3 and 1.0 per cent. solutions of ammonium, lithium, and manganese chlorides killed the plants in a few days. Sodium chloride is more injurious than the chlorides of the first group, and less injurious than those of the second. N. H. J. M.

**Transpiration and Assimilation.** By E. STAHL (*Chem. Centr.*, 1894, ii, 615—616; from *Bot. Zeit.*, 1894, 117).—When filter-paper, which has been soaked in 1 to 5 per cent. aqueous cobalt chloride, is pressed to both sides of a leaf which has stomata only on the under-side, the paper in contact with the underside of the leaf becomes red in a few minutes, whilst the other remains blue for hours.

Starch formation ceases when the stomata are closed with wax, but becomes intense when small cuts are made, indicating that in normal assimilation the gas exchange is through the stomata and not through the cuticula. The case is, however, different when much carbonic anhydride is present, and under the influence of bright light; there is then an intense starch formation, even near the closed stomata. This could be checked by covering the upper as well as the under side of the leaf with wax.

The effect of watering the plant with dilute salt water could also be shown with cobalt paper. The result was a closing of the stomata which continued even in damp air and intense sunlight. Under these conditions there was, moreover, no starch production; but there was a slight production of starch in air rich in carbonic anhydride.

N. H. J. M.

**Leaf Respiration.** By LÉON MAQUENNE (*Ann. Agron.*, 1894, **20**, 528—532).—The author and Dehérain have already drawn attention to the effect of rise of temperature in increasing respiration in leaves (*Abstr.*, 1887, 172). In the experiments now recorded, leaves of

different kinds were placed in small tubes which were then exhausted; after some time the carbonic anhydride produced was pumped out, and then pure air was let in at the ordinary pressure. After an hour or two, this was also pumped out and analysed. Leaves were, of course, selected which do not suffer under this treatment. The results, together with those obtained under normal conditions (in which the leaves were in a vacuum only as long as was necessary to collect the gas), are given in a table, showing weight of leaves, length of time in vacuum and in air, carbonic anhydride evolved in a vacuum, the composition of the final air, oxygen absorbed in the relation  $\text{CO}_2/\text{O}_2$ .

In a vacuum, a larger amount of carbonic anhydride was always produced than under normal conditions: in the case of wall-flowers, for instance, it was just double. The same holds good with regard to the absorption of oxygen. But the increased evolution of carbonic anhydride is by no means proportional to the absorption of oxygen, being sometimes higher and sometimes lower; so that the relation  $\text{CO}_2/\text{O}_2$  varies considerably. The variation is, however, the same for each species. This difference is probably due to the difference in the chemical composition of the juices of the cells. The relations between plant and air are far more complex than was supposed.

It is concluded that, during the night respiration of plants, a slow combustion of a principle takes place, the formation of which is still going on; this, in consequence, accumulates in absence of oxygen.

N. H. J. M.

**Respiration of Green and Etiolated Leaves.** By WLADIMIR PALLADIN (*Ann. Agron.*, 1894, **20**, 557—558; from *Bot. Centr.*, **58**, 375).—Attempts were made to estimate the energy of respiration of green and etiolated leaves by determining the carbonic anhydride and the relation  $\text{CO}_2/\text{O}_2$ , but without definite results. When green and etiolated leaves were floated on a sugar solution, the intensity of respiration was much increased (1 to 1.6 and 1.7), but if floated on distilled water the amount of carbonic anhydride was reduced from 70.2 to 58.1 milligrams per hour.

When the intensity is expressed in milligrams of carbonic anhydride evolved per 10 grams of proteids in the leaves, the results obtained with etiolated and green leaves were 169.3 and 163.3 milligrams respectively. There is, therefore, practically no difference if carbohydrates are present in sufficient quantity. It is concluded that proteids formed in the dark are not more energetic than those formed in the light.

The effect of sugar is natural, since carbohydrates furnish the material for respiration, whilst the respiratory energy is derived from the proteids: an excess of carbohydrates is without effect.

The respiration coefficient,  $\text{CO}_2/\text{O}_2$ , of etiolated leaves of beans (with which the experiments were made) and of lupins varies between 0.72 and 0.76. Sugar solution has no effect on the relation, but distilled water (in the dark) lowered it to 0.63—0.65.

N. H. J. M.

**Pentosans in Plants.** By GUILLAUME DE CHALMOT (*Amer. Chem. J.*, 1894, **16**, 589—611).—The author finds that pentosans are formed in the stems which are developed from barley seeds germinating in

darkness, but that there is no reason to assume that other substances which yield furfuraldehyde, or so-called oxycelluloses, are also present. By far the larger part of the furfuraldehyde-yielding compounds in these stems is, moreover, soluble in very dilute acids and alkalis, and therefore does not belong to the true celluloses.

The amount of pentosans increases in maize which is allowed to germinate in darkness, but this increase is not due to the absorption of pentosans from the soil, but to their formation from other substances present in the stems. The further the development of the young maize plants advances, the larger the quantity of pentosans formed, whereas in the case of peas which germinate in darkness the amount of pentosans at first increases but afterwards decreases. It appears, therefore, that pentosans existing in seeds are gradually decomposed and those in the stems and roots are independently formed. The transformation of pentosans, as such, is therefore only of subordinate importance. Seeds which contain much fat are almost entirely without pentosans, but these increase materially during the germination in darkness. The absence of light appears to have very little, if any, influence on the pentosans during the short time that seeds can develop in darkness. If, in addition to other nutritive matters, nitrates are applied to seeds which are germinating in darkness, the pentosans of the seeds are more readily decomposed, and less pentosans are formed in the stems and roots, which, however, contain more albuminous matter.

The author considers that pentose molecules are formed in complex molecules of hexosans (celluloses and hemi-celluloses), in which a part or all of the aldehyde groups have been bound by condensation and are therefore preserved from further oxidation. Pentose molecules are formed from hexoses by the alcoholic group at the end of the hexose molecule being oxidised to carboxyl, carbonic anhydride being simultaneously split off.

G. T. M.

**Occurrence of Oxalic acid in Beetroot.** By J. WEISBERG (*Bied. Centr.*, 1894, 23, 788; from *Oester.-Ungar. Zeits. Zuckerind. u. Landw.*, 22, 877—878).—The soluble and insoluble oxalic acid was estimated in aqueous and dilute hydrochloric acid extracts of the roots. The following percentage amounts were found.

Wt. of root (approximate).	Oxalic acid.	
	Soluble.	Insoluble.
400 grams	0.0654	0.0620
500 „	0.0461	0.0472

The amount of oxalic acid is thus variable, and the soluble oxalate (chiefly potassium salt) is present in about the same quantity as the insoluble salts.

N. H. J. M.

**Methylic Salicylate in Indigenous Plants.** By EMILE E. BOURQUELOT (*Compt. rend.*, 1894, 119, 802—804).—Methylic salicylate is present in the roots of *Polygala vulgaris*, L., from which it can be extracted by water, and also in the roots of *P. depressa* and *P. calcarica*, F. In the case of *Monotropa hypopitys*, L., which is parasitic

on the roots of pines, methylic salicylate is present in the stalks and can be extracted by means of alcohol of 90°.

When the stalks of *Monotropa* are crushed, the odour of the methylic salicylate is only perceptible after the lapse of a short time, hence it would seem that this compound is present in the form of some complex combination which is broken up by a soluble ferment. The author was unable to isolate any such ferment, but fragments of the stalks of *Monotropa* or of the roots of *Polygala* have the power of splitting up amygdalin in aqueous solution. C. H. B.

**Occurrence and Rôle of Myrosin in Plants.** By W. SPATZIER (*Bied. Centr.*, 1894, **23**, 785; from *Bot. Centr.*, 1893, **55**, 303; and *Inaug. Diss.*, Erlangen, 1893).—The rôle of myrosin is the production of glucosides. It is, however, not known which glucosides are found besides potassium myronate and sinalbin, what products occur, and whether the products have any other object besides that of protection from external attacks. The manner in which myrosin is formed and whether it has any other function is still uncertain.

N. H. J. M.

**Richness of Soil in Nitrogen after the Cultivation of Various Plants.** By PROVE (*Ann. Agron.*, 1895, **21**, 46—47; from *Zeits. landw. Ver. Bayern*, 1893, **83**, 59 and 101).—Various plants were grown in clayey sand manured with potassium sulphate and superphosphate, and contained in five pots. There were also two cylinders without vegetation; the soil of one of these was covered with dead moss. The total nitrogen was in each case rather over 7 grams. There was a loss of nitrogen in the soil in every case, and also a loss of total nitrogen. The losses of nitrogen were as follows (1) in soil (2) in total nitrogen (grams).

	Maize.	Rye.	Buck-wheat.	Dwarf beans.	Lupins.	Clover.
(1.)	2·313	2·013	2·189	1·887	1·436	1·403
(2.)	2·029	1·815	1·951	0·862	0·161	0·538

	Horse beans and vetches.	Bare soil.	
		With moss.	Exposed.
(1.)	1·489	0·498	0·217
(2.)	0·106	0·498	0·217

Whilst the *Leguminosæ* yielded about four times as much nitrogen as the non-leguminous plants, they withdrew much less from the soil, and if incorporated with the soil there is less loss than when the soil was kept without vegetation. Frank is wrong in attributing to all phanerogams the power of fixing elementary nitrogen.

N. H. J. M.

**Analyses of Silesian Soils.** By B. SCHULZE (*Bied. Centr.*, 1894, **23**, 728—731; from *Der Landwirt.*, 1894, Nos. 50 and 81).—The author made analyses of 168 normal Silesian arable soils. The sampling and analyses were all made according to one plan, and the results are, therefore, all comparable with one another. Nitrogen, phosphoric acid, potash and lime were estimated, and in many cases magnesia and

iron, &c. Taking the minimum amounts of nutritive constituents which a soil should contain as follows: nitrogen and phosphoric acid, 0.1; potash, 0.08; and lime, 0.25 per cent. in dry soil; the soils are divided under each constituent into those which are deficient and those which are not. A considerable number of soils were deficient in nitrogen, and to remedy this green manuring is recommended for the lighter soils. Phosphoric acid is very important to obtain good yields and good quality of grain and roots. Potash was deficient only in 19 per cent. of the soils, lime in 53 per cent. N. H. J. M.

**Experiments on Wheat and Barley at Grignon in 1894.** By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1894, 20, 561—585).—In order to examine the roots of wheat at different periods of growth, wheat was sown on a bank from which the soil was removed from time to time so as to expose the roots. The first examination was on the 15th December, 1893. The character, length, &c., amount of dry substance as compared with the above-ground growth were noted, and also the amounts of nitric acid in tops and roots. The weight of dry root per cent. of above-ground growth diminished from 73 to 27 by the 13th of May. The nitric acid in the roots diminished continuously, but increased in the above-ground growth until the end of April; by the 13th of May it was less, and a month later there was a great decrease both in above-ground growth and in the roots.

In order to determine the respiratory energy of wheat leaves, which, owing to the short time they exist, might be expected to be great, air was passed over leaves contained in a tube, and analysed by Reissert's method. The results of the experiments, which were made on the 6th June, showed an absorption of 0.19 gram of carbonic anhydride in five hours by a leaf weighing (fresh) 0.353 gram. In a subsequent experiment, however, (22nd June) the absorption was only 0.002 gram by a leaf weighing 0.4 gram. The experiments will be repeated. The stems, when still green, give off carbonic anhydride instead of absorbing it; ears of the average weight, 3.74 grams, gave up 0.010 gram of the gas in five hours.

Although from July wheat plants no longer possess organs able to produce vegetable matter, the weight of the crop still increases. The following amounts of dry produce were obtained from 10 sq. metres:—30th June, 875 grams; 6th July, 977.8 grams; 16th July, 1055.7 grams; 26th July, 1312.4 grams; and 6th August, 1107 grams.

The second part of the paper gives the results of experiments on different varieties of wheat and barley under the influence of different manures. N. H. J. M.

**Effect of Manure, Season, and Seed on the Composition of Rye Grain.** By M. FISCHER (*Chem. Centr.*, 1894, ii, 173—174; from *Ber. u. d. physiol. Lab. landw. Inst. Univ., Halle*, Heft 10, 34).—Nitrogen-free extract and fat are affected more by the season than by manures; moisture and sunshine during the development of the grain giving rise to a high percentage of the former. Richness in fat is accompanied by a low percentage of nitrogen-free extract, and seems to be favoured by dung and by exclusively nitrogenous manure.

The lowest percentage of ash was also obtained under the influence of nitrogenous manure.

An abundant straw production, whether caused by season, by stable manure, or by an exclusively mineral manure, results in low percentage of nitrogen. The highest percentage of proteids was obtained with dung, high results with nitrogenous manure alone, and moderate proteid production with artificial nitrogenous and mineral manures together. Unmanured rye is rather rich in nitrogen.

The percentage relation of pure protein to total nitrogen varies generally with the amount of ash, so that with exclusively mineral manure the greatest amount of the nitrogen is in the form of protein; with exclusively nitrogenous manure, the least. The greatest and smallest absolute amounts of actual protein are produced under the influence of dung and of purely mineral manure respectively; the indigestible nitrogenous matter is fairly constant with the same season, seed, and soil. Grain of low sp. gr. has not only a high percentage of indigestible protein-nitrogen, but its relation to total nitrogen is also high. Very low total nitrogen and very high percentage of ash do not necessarily indicate an especially high relation of digestible protein-nitrogen to total nitrogen. When the total nitrogen is high and the ash percentage low, the nitrogen of the digestible protein is usually low. The employment of dung gives the highest amount of digestible protein, both absolute and in relation to the indigestible protein. Good results are also obtained by means of a suitable mixture of artificial nitrogenous and mineral manures.

N. H. J. M.

**Manuring Experiments with various Phosphates and Nitrogenous Substances.** By LARS F. NILSON (*Bied. Centr.*, 1894, 23, 737—746; *Midd. f. k. landtbr.-akad. exper.*, 1894, No. 24).—In 1889—91 large quantities of apatite were found in North Sweden. The phosphates cannot, however, be worked with advantage in the ordinary manner, but may be treated with the iron ores in the Thomas process. A product, obtained in the course of provisional experiments, in which the apatite could not be mechanically separated from the iron ores, was treated with lime in an ordinary furnace. The resulting slag, when compared with basic slag, as manure for barley was found to have very little effect. After being heated at an intense white heat, it proved to be quite equal to basic slag. As compared with superphosphate, 2 parts of the apatite product (and of basic slag) gave about the same results as 1 part of superphosphate; this is in accordance with Wagner's experiments with basic slag. Comparative experiments were next made with various bone meals—Russian and Swedish steamed bone meals, meal from coprolites, burnt and fused coprolites, and fused bone ash. The ordinary bone meals proved to have but little value, the fused bone ash was as effective as basic slag, or more so, whilst the burnt coprolites had least effect of all, owing to the amount of silica (15 per cent.) they contained and the deficiency of calcium carbonate. If the coprolites were heated with sufficient lime, they would probably be as effective as fused bone ash. In the second and third years of the experiments with bone meal, there was a diminution in the yield of barley.

Experiments on the effect of various phosphates on the composition of the barley grain were next made, the manures selected being basic slag (100 to 200 kilos. per hectare), potassium orthophosphate, potassium metaphosphate, and superphosphate (50 to 100 kilos.). The three soluble phosphates gave equal increase of produce. As regards the amount of protein in the grain, there was a decrease which was greater the greater the amount of phosphate applied; without manure, the grain contained 21·5 per cent. of protein, whilst with soluble phosphates (100 kilos. per hectare) it was only about 9 per cent., and with basic slag (200 kilos.) about 12 per cent. The soil with which the experiments were made was a peaty soil very rich in nitrogen, and it had also an application of nitrate (25 kilos. per hectare).

Similar experiments made with sugar-beet showed that superphosphate and potassium phosphate gave only 0·6 the amount of sugar that was obtained with the corresponding amount of basic slag.

In the next experiments, the effect of herring-guano on oats as compared with sodium nitrate was investigated. A fine, sandy soil, to which potassium sulphate and basic slag were added, was employed. The herring-guano gave about 80 per cent. of the increase produced by Chili saltpetre containing the same amount of nitrogen; but it is possible that its action might extend to subsequent crops. In absence of potash and phosphoric acid, the effect of herring-guano, as compared with Chili saltpetre, is still less.

The results of the last experiments in which barley, oats, and peas were manured with phosphates, potassium sulphate, and sodium nitrate, indicate that it is the phosphates mainly which increased the yields in the soil employed (peaty soil from Gothland); peas seemed benefited by potash also. The pea straw was increased by the application of nitrate, but the amount of grain diminished.

N. H. J. M.

**Varying Composition of Malt: Means of Regulating the Degree of Fermentation.** By E. EHRLICH (*Bied. Centr.*, 1894, **23**, 840—843; from *Bierbrauer*, 1894, **25**, 339, 411, 435).—The composition of malt varies with the season; the malts of 1893, for instance, were poorer in maltose than those of 1892. Barley and malt produced in different districts also vary. As examples, results obtained with Pilsen, Vienna, and Munich malts in 1892 and 1893 are given. The method now described for regulating the degree of fermentability, especially in the thick mash process, depends on the solubility of diastase in water and on the behaviour of diastase at higher temperatures. At 50° there is an energetic action of diastase on the starch; the action is still stronger at 55° to 64°, at which temperatures most sugar (about 75 per cent.) is formed in the shortest time. At higher temperatures, the starch is still more quickly converted, but the amount of sugar diminishes owing to the production of dextrin. Above 75°, the production of sugar diminishes quickly.

N. H. J. M.



## Analytical Chemistry.

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**Difficulty in the Detection of Chlorine in Methylene Blue.** By WILHELM LENZ (*Zeit. anal. Chem.*, 1895, **34**, 39—48).—A solution of methylene blue hydrochloride of the formula  $C_6H_{17}N_3S.HCl$  gives no precipitate with silver nitrate. On then adding nitric acid, a small portion of the chlorine is precipitated, and, on boiling with nitric acid, a larger portion, but in no case could the theoretical amount be obtained. The whole amount (11.4 per cent. of  $HCl$ ) was, however, obtained when the substance was fused with sodium hydroxide and potassium nitrate before treatment with silver nitrate, or was oxidised in the wet way by the following process, which is of general applicability to organic substances. The extremely finely powdered substance is mixed in a porcelain mortar with dilute soda to a thin paste, and finely-powdered potassium permanganate is added in small portions until the colour of the mixture is that of permanganate without a trace of green. The mass, which has become solid, is mixed with more soda, and dissolved in hot water; the excess of permanganate is reduced with alcohol and the filtered liquid, after acidification with nitric acid, is precipitated with silver nitrate. A similar method serves for the estimation of sulphur, but it is necessary to add the permanganate so slowly that rise of temperature is avoided, and finally to add a considerable excess so that a saturated solution is produced. After remaining for about a week, the mixture is heated with excess of strong hydrochloric acid until all chlorine is expelled. The sulphur in many substances may be estimated by this method, but it fails with others, notably with "saccharin." Specimens of methylene blue (exclusive of those containing zinc chloride) formerly found by the author to give the chlorine reaction with silver nitrate, must, he assumes, have contained more hydrochloric acid than corresponds with the above formula.

Methods of distinguishing methylene blue from other coal-tar dyes are given in the paper. M. J. S.

**Chlorine in the Gastric Secretion.** By HENRI LESCEUR (*Compt. rend.*, 1894, **119**, 909—912).—The chlorine present in the gastric secretion as (1) hydrochloric acid, (2) inorganic chlorides, and (3) organic chlorine, is determined according to the method of Hayem and Winter, by estimating the chlorine in three separate quantities of the liquid (a) after adding sodium carbonate, evaporating and heating strongly, (b) after evaporating at  $100^\circ$ , then adding sodium carbonate and heating, and (c) after evaporating and strongly heating without addition of sodium carbonate. The author heats the liquid in a glass flask through which passes a current of air, the issuing gas being passed through a wash-bottle. The products volatilised at  $100^\circ$  are first collected, and afterwards the products of carbonisation.

The two methods gave identical results as regards the hydro-

chloric acid, provided that a temperature of  $100^{\circ}$  is not exceeded. The results for organic chlorine are lower by the author's method, but the difference tends to disappear if the flask is heated above  $200^{\circ}$ . It would seem that part of the chlorine is volatilised in the form of ammonium chloride owing to pyrogenic reactions between the proteids and the sodium chloride.

The author concludes that the chlorine present in the gastric juice in the form of hydrochloric acid is capable of exact estimation, but the same precision does not obtain in the case of the combined chlorine, and especially of the so-called "organic" chlorine.

C. H. B.

#### **New Gasometric Method of Estimating Nitrogen in Nitrates.**

By FR. GANTTER (*Zeit. anal. Chem.*, 1895, **34**, 25—32).—The measurement of the nitric oxide evolved by the action of copper and sulphuric acid on a nitrate, yields satisfactory results only when the quantity of nitrate is not too small. The reaction  $\text{N}_2\text{O}_5 + \text{P}_2\text{O}_5 + 2\text{NH}_4\text{Cl} = 2\text{N}_2 + \text{P}_2\text{O}_5 + 3\text{H}_2\text{O} + 2\text{HCl}$  is, however, applicable to very minute quantities. It is quantitatively complete, and, owing to the evolution of twice as much nitrogen as is contained in the nitrate, it is very sensitive. The author employs the gas volumeter formerly described (*Abstr.*, 1894, ii, 26), but with the introduction, between the tubes *a* and *b* of the reaction flask, of a special absorption vessel, containing soda to arrest hydrogen chloride. To avoid calculation, 289 milligrams of the substance is used: 5 c.c. of water expelled from the apparatus then corresponds with 1 per cent. of nitrogen as nitric acid. This quantity, contained in 3 c.c. of solution, is placed in the reaction flask with 0.5 gram each of crystallised ammonium chloride and crystallised phosphorus acid, and 2 c.c. of sulphuric acid (2 vols. of concentrated acid with 1 vol. of water). In the pipette B (*loc. cit.*) is placed 5 c.c. of the same acid. After equalising the temperature, the reaction flask is very slowly and carefully warmed. Should the mixture become yellow, or red fumes be evolved owing to too rapid heating, the results are inaccurate. When evolution of gas ceases, the additional sulphuric acid is slowly dropped in and the mixture is finally raised to boiling and boiled vigorously for a few minutes, but not so long as to produce a brown colour from the concentration of the sulphuric acid. The method is very suitable for estimating nitrates in natural waters, and the test analyses with pure substances gave very favourable results.

M. J. S.

**Estimation of Phosphoric acid by Titrating the Yellow Precipitate.** By B. W. KILGORE (*J. Amer. Chem. Soc.*, 1895, **16**, 765—772).—Methods based on the principle of titrating the yellow precipitate have been described by Thilo, Manby, Handy, and others. The process gives good results, but it is often difficult to prevent an admixture of free molybdic acid, which, of course, renders the result untrustworthy. By operating, however, as follows, the author obtained good results.

Two grams of the phosphate is dissolved in 30 c.c. of nitric acid and 5—10 c.c. of hydrochloric acid, and diluted to 200 c.c.; 20 or 40 c.c. is now put into a beaker, mixed with ammonia until

a precipitate just begins to form, and diluted to 75 c.c. If much of the nitric acid was lost when making the solution, 10—15 grams of ammonium nitrate had better be added. After heating on the water bath to 60°, excess of ammonium molybdate solution is added, and after standing for five minutes the liquid is filtered and the precipitate washed by decantation until the washings are no longer acid. The filtration is best carried out by using a Hirsch funnel in connection with a filter pump. The precipitate is then dissolved in excess of standard potash and titrated with standard nitric acid.

The molybdate solution is made by dissolving 100 grams of molybdic acid in 417 c.c. of ammonia (sp. gr. 0.96), and pouring this into 1250 c.c. of nitric acid (sp. gr. 1.20). The solution should be filtered before use. L. DE K.

**Volumetric Estimation of Phosphoric acid.** By R. SEGALLE (*Zeit. anal. Chem.*, 1895, **34**, 33—39).—Direct acidimetric titration of phosphoric acid, with whatever indicator, does not furnish exact results. The following small modification of Glücksmann's method is both rapid, convenient, and accurate. To the solution of the phosphoric acid, a liberal known excess of a standard ammonia solution is added; then sufficient of a perfectly neutral solution of magnesium sulphate. The mixture is made up to a known volume, vigorously shaken, and immediately filtered through a dry filter. The excess of ammonia is titrated, and 1 mol. of phosphoric acid is calculated for 3 mols. of ammonia which have undergone neutralisation.

M. J. S.

**Estimation of Soluble Phosphate.** By VINCENT EDWARDS (*Chem. News*, 1895, **71**, 69—70).—The author finds that allowing the precipitate of ammonium magnesium phosphate to settle during either 1½ or 48 hours does not give rise to any variation of importance in the numbers obtained for soluble phosphate in superphosphate; he regards 2½ hours as sufficient to allow for the settlement.

D. A. L.

**Estimation of Arsenic and Sulphur.** By LEONARD DE KONINGH (*Ned. Tydschr. v. Pharmacie, &c.*, 1894, 365—367; 1895, 18—20).—Sulphur may be conveniently oxidised to sulphuric acid by the use of alkaline potassium permanganate. About 0.5 gram of the sample is dissolved in a few c.c. of saturated hot aqueous potash, which is generally completely free from sulphate, the solution is diluted with about 100 c.c. of boiling water, and powdered potassium permanganate is stirred in until the liquid acquires a greenish-red colour. In this way, the sulphur is completely oxidised, and, after heating with excess of hydrochloric acid until a colourless solution is obtained, the sulphate may be precipitated as usual with barium chloride. In arsenic analysis, it is customary to weigh first as sulphide, after removing as far as possible any free sulphur by means of carbon bisulphide, and then to estimate the sulphur in the precipitate. The author advises treating the filter and the precipitate with alkali and permanganate in the way described, the oxidation being instantaneous. The clean part of the filter may be first cut off.

If a mixture of arsenious acid and excess of sulphur is boiled with aqueous potash until everything is dissolved, and then, after cooling, reprecipitated by hydrochloric acid, the precipitate does not contain all the arsenic, as may be proved by passing a current of hydrogen sulphide through the filtrate. If the alkaline solution is boiled with addition of small quantities of basic bismuth nitrate, the bulk of the sulphur is readily removed. This reaction has not been used quantitatively, as the bismuth sulphide is supposed to retain arsenic, but the author states that all the arsenic remains in solution, and may be estimated by acidifying with hydrochloric acid and at once adding excess of bromine. The remaining sulphur is quickly oxidised, and the arsenic passes into the higher state of oxidation, and may then be precipitated by adding ammonia and magnesia mixture. As regards the last reagent, the author states that when stale it is a very treacherous one, often causing a precipitate of magnesium hydroxide, as may be noticed by the occasional bulky appearance of the magnesium ammonium arsenate. The reagent should always be tested to see whether it yields a precipitate on merely adding it to dilute ammonia; should this be the case, it must be mixed with more ammonium chloride. But the safest plan is to filter off the mother liquor, and then redissolve the arsenical precipitate in dilute hydrochloric acid and reprecipitate with ammonia.

The author communicates a test experiment with a mixture of arsenious acid and free sulphur, containing also a small quantity of orpiment. The result of the arsenic estimation was the same whether weighed as arsenic sulphide with subsequent estimation of sulphur, or by the bismuth process. The estimation of the sulphur was controlled by extraction with carbon bisulphide. Allowing for the sulphur existing as orpiment, the result was very satisfactory.

L. DE K.

**Estimation of Alkali Hydroxides and Carbonates in the Presence of Alkali Cyanides.** By J. E. CLENNELL (*Chem. News*, 1895, **71**, 93—94).—These estimations may be effected by titrating the cyanide directly with silver nitrate; then, in the same solution, with phenolphthalein as indicator, estimating the hydroxide and half the carbonate by titrating with hydrochloric acid. The total alkali is titrated directly with hydrochloric acid, using methyl-orange as indicator. The alkalinity due to the cyanide, hydroxide, and carbonate respectively being calculated from these numbers.

D. A. L.

**Decomposition of Sulphates by Ammonium Chloride.** By MASUMI CHIKASHIGÉ (*Chem. News*, 1895, **71**, 17).—It is observed that when a mixture of magnesium or sodium chloride with ammonium chloride, ammonia and very little sulphuric acid is evaporated and heated sufficiently strongly to expel the ammonium salts, some sulphuric acid still remains in the residue; this must be taken into consideration in analytical operations involving such treatment.

D. A. L.

**Analysis of Sodium Peroxide.** By LEONARD ARCHBUTT (*Analyst*, **20**, 1895, 3—5).—After trying the permanganate process with but

indifferent success, the author succeeded very well by using cobalt nitrate.

The sample is weighed into a small tube which is placed in a flask attached to a Lunge's nitrometer. In the flask, is put 5 c.c. of water and a drop of cobalt solution; the mercury is then levelled, and on bringing the peroxide into contact with the reagent, the available oxygen is quantitatively liberated and its volume ascertained as usual.

L. DE K.

**Estimation of Calcium Oxide in Quicklime.** By WINTHROP E. STONE and F. C. SCHEUCH (*J. Amer. Chem. Soc.*, 1894, **16**, 721—723).—One gram of the finely powdered sample is shaken for twenty minutes with 150 c.c. of a 10 per cent. solution of saccharose. Calcium oxide soon dissolves, whilst calcium carbonate, magnesia, ferric oxide and alumina are quite insoluble. The solution is filtered, and the clear filtrate titrated with standardised hydrochloric acid. The test analyses prove the commercial accuracy of the process. L. DE K.

**Analysis of Zinc and Copper Alloys.** By H. N. WARREN (*Chem. News*, 1895, **71**, 92).—Brass filings are dissolved in strong sulphuric acid, the solution diluted, some magnesium ribbon introduced, and a temperature of 38° maintained, until all the copper is precipitated. This is collected, washed, weighed, and, if other metals of the same group are suspected, further examined. The solution is boiled with strong sodium acetate, the basic ferric acetate filtered off, and the zinc, now present as acetate, precipitated from the filtrate by means of rods of magnesium. D. A. L.

**Analysis of American Refined Copper.** By HARRY F. KELLER (*J. Amer. Chem. Soc.*, 1894, **16**, 785—789).—The author's method is a slight modification of the thiocyanate process introduced by Hampe; 25 grams of the sample is dissolved in a mixture of 200 c.c. of water, 45 c.c. of nitric acid (sp. gr. 1.21), and 25 c.c., or more, of strong sulphuric acid. When, on heating, no more nitric fumes are given off, the liquid is diluted with 200 c.c. of water, and heated to 40°. A rapid current of sulphurous anhydride is now passed through until all the nitric acid is destroyed, when the liquid becomes turbid owing to the precipitation of silver, selenium and tellurium. After adding a drop of hydrochloric acid to precipitate the last traces of silver, the liquid is allowed to remain for 24 hours in a warm place, and then passed through a small filter. The filtrate may contain bismuth, antimony, iron, nickel, and cobalt.

The sediment is composed of gold, silver, silver chloride, selenium, tellurium, perhaps lead sulphate and traces of bismuth and antimony. To determine the elements in the filtrate, the greater part of the copper must first be removed. For this purpose, a measured amount of standard potassium thiocyanate (1 c.c. = 0.05 cu.) is gradually added, whilst a current of sulphurous anhydride is passed into the liquid. It is preferable to leave a trace of the copper in solution. The mixture is now made up to 2 litres, and after the precipitate has settled, an aliquot part, say 1800 c.c., is filtered. The precipitate may be taken to occupy 16 c.c., so that the total volume of liquid is

really 1984 c.c. After expelling the excess of sulphurous anhydride by boiling, the metals are precipitated by hydrogen sulphide and further separated by the usual analytical methods. The insoluble portion is detached as completely as possible from the filter, which is treated with fuming nitric acid in a small porcelain dish; the detached portion is then added and treated with the acid until completely oxidised. After evaporating the excess of acid, the residue is digested with dilute hydrochloric acid to separate the silver. In the filtrate, the tellurium and selenium are precipitated by means of hydroxylamine hydrochloride by aid of a gentle heat. After first weighing the mixed elements on a tared filter, an attempt was made to separate the tellurium by fusing the mixture in a current of hydrogen with potassium cyanide; the aqueous solution was then exposed to the air, causing most of the tellurium to separate.

Gold, lead and the traces of antimony and bismuth are estimated by the ordinary methods. L. DE K.

**Examination of Rose Oil for Geranium Oil.** By ROBERT JEDERMANN (*Zeit. anal. Chem.*, 1895, **34**, 51—53).—The author controverts the statements of Panajotow (*Abstr.*, 1891, 1855), as to the possibility of detecting geranium oil in oil of roses by either Schiff's reagent or Hager's sulphuric acid test, and states that the oil prepared from white roses yields with the latter a turbidity resembling that produced by geranium oil, whilst with the former he has only known a single case out of hundreds in which a blue colour was not produced after a few hours. The specific gravity test is equally untrustworthy, since the gravity of rhodinol (0.873—0.8735), the elæoptene of rose oil, and its only odoriferous constituent, approaches so closely that of geranium oil (0.882—0.895); the proportion of the valueless stearoptene, which is of lower gravity, varying from 7 to 30 per cent. according to conditions of soil and preparation. The action of rhodinol and geraniol on polarised light is also identical, and he regards them as isomeric substances. At the present time, no trustworthy chemical means exists for detecting this adulteration.

M. J. S.

**Procedure in Fehling's Titration.** By ARTHUR BORNTÄGER (*Zeit. anal. Chem.*, 1895, **34**, 19—25).—Of the two methods of procedure studied by Soxhlet, many text-books and official prescriptions adopt that in which undiluted Fehling's solution and a sugar solution of 0.5—1 per cent. are employed. This involves the use of at least 50 c.c. of Fehling's solution for each titration, and the evaporation of weaker sugar solutions. Good results can be obtained by the use of only 10 c.c. of the copper solution diluted with four volumes of water, and, since the water may be derived from the sugar solution itself, this method permits the employment without concentration of sugar solutions of only 0.1 per cent., such as occur in the analysis of fully fermented wines. The mixture should in any case have a total volume of 55—60 c.c. A flask is to be preferred to a basin. In the preliminary titrations, in which the colour of the supernatant liquid is used as a guide, the flask should rest on a white ground, and the sugar solution may be added to the hot

copper solution, but the final result should be deduced from the mean of two titrations, differing by only 0.1 c.c., in which the mixtures are made in the cold, and, after boiling for exactly two minutes and filtering, one filtrate gives a brown colour with acetic acid and ferrocyanide, whilst the other does not. A thick paper, or else double or triple filters, should be used to obtain a filtrate perfectly free from cuprous oxide; only a few c.c. of the filtrate should be collected, and the greatest rapidity is essential in order to entirely avoid reoxidation of the precipitate. Sugar solutions of more than 1 per cent. must be diluted to that strength before filling the burette, otherwise errors of reading influence the result too greatly. The copper solution and alkaline tartrate should be preserved separately, and if the tartrate solution is filtered before adding the alkali, it remains unaltered longer. The results should always be expressed in terms of "invert sugar," of which, according to Soxhlet's determination, 10.31 c.c. of a 0.5 per cent. strength reduce exactly 10 c.c. of normal Fehling's solution. Working as above, the use of a sugar solution of only 0.05 per cent. leads to an error not exceeding 4—5 per cent. of the whole amount.

M. J. S.

**Ratio of *d*-Glucose to Levulose in Sweet Wines and Honey, and the Use of this Ratio for Detecting Adulteration.** By J. KÖNIG and W. KARSCH (*Zeit. anal. Chem.*, 1895, 34, 1—18).—The proportions of the two sugars were estimated both by the method of Soxhlet (*Abstr.*, 1880, 758) and that of Neubauer (*Abstr.*, 1877, 641), the results of which agree closely in the case of wine and must. In unfermented must, the *d*-glucose was found to exceed the levulose in the ratio of 100 : 77—84. Fermentation, whether natural or induced by the addition of yeast, removed the *d*-glucose more rapidly than the levulose, so that the proportions speedily became inverted. Cane sugar added to wine is inverted by the acids present, and the fermentation of the two glucoses produced follows the same course as in natural wine. The only conclusion derived from the research is that if a sweet wine contains considerably more levulose than *d*-glucose, it is probably a fermented wine; if, on the other hand, the *d*-glucose preponderates largely, it is likely that no fermentation has taken place.

For the examination of honey, it is necessary to remove the dextrinoid substances. For this purpose 40 grams of honey is diluted with water to 40 c.c., and 20 c.c. of this mixture is slowly made up to 250 c.c. with absolute alcohol. After 2—3 days, the solution is filtered from the precipitate, and portions of it are used (after expulsion of the alcohol) for the titrations and polarisation. In the case of honey, Neubauer's method gave results differing widely from those of the Soxhlet-Sachsse titrations, the divergence being greatest in those samples (of honey from flowers) which gave the largest amount of precipitate with alcohol. It must therefore be assumed that honey contains constituents possessing reducing powers and optical properties which differ from those of *d*-glucose and levulose, and, in particular, that a strongly dextrorotatory substance is present. The ratio of *d*-glucose to levulose, as estimated by titration, varies

largely in different specimens of genuine honey, so that as much as 25 per cent. of starch sugar might be added to certain samples without exceeding the proportion of *d*-glucose found in others. All the natural honeys examined (including that from conifers) show, however, lævorotation after removal of dextrin. Dextrorotation under these circumstances would indicate the addition of starch sugar.

M. J. S.

**Comparison of Methods for the Estimation of Starch.** By WINTHROP E. STONE (*J. Amer. Chem. Soc.*, 1894, **16**, 726—733).—The author has tried, side by side, five different processes for the estimation of starch, including four inversion processes and the baryta process. [The latter method, as described by the author, differs considerably from the original method.—Abstractor.] The results were in every case very satisfactory when dealing with pure starches, but all methods failed when applied to meals and fodders. Hay and cotton-seed meal, for instance, which gave no iodine reaction for starch, still should have been credited with containing large amounts of that substance when tested by the quantitative methods, particularly if analysed by the baryta process.

This leads to the unavoidable conclusion that besides starch, other substances are often present which behave quantitatively like starch; these, no doubt, belong to the pentosans.

L. DE K.

**Estimation of Woody Fibre in Fodders.** By A. P. AITKEN (*Analyst*, 1895, **20**, 35—37).—The great drawback of the old *acid and alkali* process for the estimation of woody fibre is that it only gives concordant results when the strength of the solutions, and also the time of boiling, is always the same. The strength, however, increases during the boiling, and it is therefore necessary to almost constantly add boiling water to replenish the loss caused by evaporation. Although this may be avoided by using a reflux condenser, the danger of frothing is also to be considered. The author now proposes to put the liquids into beakers covered with watch-glasses, and to immerse them in a steam bath. In this manner the temperature of boiling water is maintained, whilst practically no evaporation takes place.

L. DE K.

**Bell's Analyses of Genuine Milk.** By JOHN F. LIVERSEEGE (*Analyst*, 1895, **20**, 7—12).—The author states that milk analysed by Bell's process may show from 0.4 per cent. less to 0.26 per cent. more fat than when analysed by the specific gravity and total solids method.

The great bulk of Bell's analyses are, however, quite in accordance with the generally accepted ideas about the composition of average natural milk.

L. LE K.

**The Keeping of Milk for Analysis.** By M. KÜHN (*Bied. Centr.*, 1895, **24**, 68; *Der Landwirt.*, 1894, Nos. 40—43).—For keeping milk only a few days, 0.2 to 0.3 gram of potassium dichromate is added per litre; otherwise about 1 gram is employed (*Alén, Bied. Centr.*, **23**, 121). Milk so treated gives turbid solutions when



examined by Soxhlet's areometric method, and the separation of the ethereal solution is sometimes difficult. To avoid this it is proposed to put a cotton-wool plug (10—20 mm. long) in the tube which dips into the ethereal fat solution, and to force the fat solution into the apparatus by pouring water in, instead of by means of bellows (compare *Milchzeit*, 1891, No. 40).

The sp. gr. of the milk can be determined if the amount of potassium dichromate added is known. The addition of 1 gram of the salt to 1 litre of milk raises the sp. gr. "one degree" (*sic*).

N. H. J. M.

**The Twitchell Method for Estimating Rosin in Soap.** By THOMAS EVANS and I. E. BEACH (*Amer. Chem. Journ.*, 1895, 17, 59—67).—The authors have noticed that rosin generally contains from 6—9 per cent. of unsaponifiable matter which, no doubt, accounts for the indifferent results obtained by some investigators when using Twitchell's process (Abstr., 1892, ii, 389; 1893, ii, 609) for the estimation of rosin in a mixture of the same with fatty acids. To render the process a really good one, from a soap manufacturer's point of view, a good method for the estimation of this unsaponifiable matter will have to be discovered.

L. DE K.

**Gladding's Process for Estimating Rosin in Soap.** By LEONARD ARCHBUTT (*Analyst*, 1895, 20, 6—7).—This process is seriously interfered with by the presence of unsaponified fat. Gladding's directions as regards this matter are not stringent enough, and the author therefore advises either to boil the sample with excess of alkali, or to remove the fat from its aqueous solution by shaking with ether. The soap thus purified is then decomposed with acid and the liberated fatty acids treated according to Gladding's directions.

L. DE K.

**Estimation of Glycocine.** By MAX GONNERMANN (*Pflüger's Archiv*, 1894, 59, 42—46).—Fischer (Abstr., 1894, ii, 336) has introduced a method of estimating glycocine by converting it into hippuric acid; he, moreover, finds that 100 grams of gelatin yields 9 grams of hippuric acid or 3.78 of glycocine. The present research confirms the value of this method so far as glycocine is concerned, but with gelatin the result was different, being much higher; the number given is from 7.73 to 8.44 instead of 3.78.

W. D. H.

**Table for the Estimation of Urea by Riegler's Method.** By LUDWIG VANINO (*Zeit. anal. Chem.*, 34, 55—57).—This is a table for the reduction to milligrams of urea of the volume of gas ( $\text{CO}_2 + \text{N}$ ) evolved by the action of Millon's reagent (Abstr., 1894, 166).

M. J. S.

**Optical Method for Estimating Albumin and Uric acid in Urine.** By A. CLARENCY (*J. Pharm.*, 1894, [5], 30, 484—487).—The methods at present used for the estimation of albumin and of uric acid in urine are difficult and tedious. The author obtains very good results by means of the Aglot apparatus for tannin as follows:

I. *Albumin*.—20 c.c. of the urine is filtered, and, if not yet perfectly

clear, 0.5 c.c. of N/10 silver nitrate is added and the liquid refiltered; 12 c.c. of the clear urine is then introduced into a graduated tube, 8 c.c. of a 12.5 per cent. solution of trichloroacetic acid added, the whole shaken five or six times, allowed to remain three minutes, and again similarly shaken. The liquid is then introduced into the Aglot apparatus and examined with the opal glass as usual. The thickness  $E$  in millimetres of liquid necessary to extinguish the light, multiplied by the quantity  $Q$  of albumin in grams per litre is a constant  $C$ , which is, under the above conditions, 8.2. Therefore  $Q = 8.2/E$ . The trichloroacetic acid may be replaced by Esbach's solution, in which case the constant becomes 5.0.

II. *Uric acid*.—The urine to be tested is agitated strongly to bring the urates and free acid into suspension, 25 c.c. is rapidly measured and introduced into a flask, 0.3 gram of pure sodium carbonate is added, and the whole heated on a water-bath for a quarter of an hour to bring the uric acid and urates into solution. After cooling and filtering, 20 c.c. of this liquid is measured into a flask, 10 c.c. of a solution of copper thiosulphate added, and the mixture left for five minutes. It is then introduced into the Aglot apparatus and tested. In this case, the constant is equal to 5.6, and the quantity of uric acid in grams per litre is equal to  $5.6/E$ . The copper thiosulphate being very unstable must be prepared as needed from the following three stable solutions. A, 40 grams of Rochelle salt, 20 grams of sodium thiosulphate and water to 250 c.c. B, copper sulphate 3.5 grams and water to 250 c.c. C, syrup of glucose of 36°. 3 c.c. of A, 7 c.c. B and 10 c.c. of C are mixed together.

Very accurate results are obtained and the two estimations may be performed in about half an hour. L. T. T.

**Analysis of India-rubber.** By ROBERT HENRIQUES (*Chem. Zeit.*, 1894, 18, 905—906).—The author, in reply to Terry (*Jour. Soc. Chem., Ind.*, 1892, 11, 972) and Lobry de Bruyn, states that an appreciable loss of india-rubber is caused by the solubility of the same in alcoholic alkali. The alcohol should therefore always be expelled and the residue treated with water (*Abstr.*, 1893, ii, 399). L. DE K.

**Analysis of Rubber Goods.** By CARL O. WEBER (*Chem. Zeit.*, 1894, 18, 1003—1005; 1040—1041; 1064—1069).—The author has given an interesting process for the analysis of rubber goods. It may be briefly described as follows:—The finely-divided sample is first treated with acetone which dissolves fatty and sulphurised oils, mineral oils, rosin oil, natural and added resins, paraffins, free, and in part, combined sulphur. The residue is exhausted with boiling alcoholic soda which dissolves *faktis* and any sulphur or chlorine contained therein. After drying, the mass is extracted with cold nitrobenzene which dissolves asphalt and any sulphur therein contained. The extraction is then repeated with boiling nitrobenzene which dissolves the rubber and any vulcanising sulphur. After this, the residue is boiled with water and the solution tested for starch, whilst the insoluble matters will now consist of the mineral matter with any lamp-black and a little sulphur. As it is not practicable to recover the dissolved matter from the

alcoholic soda or the nitrobenzene, the insoluble matter must each time be weighed. The adhering nitrobenzene may be easily removed by washing with benzene.

The author also gives a delicate test for the presence of red lead. The finely-ground sample is moistened with a solution of aluminium chloride in ether and then heated in an air bath for two hours at 120°. If red lead is present the rubber becomes hard and brittle and emits an odour of chlorine.

L. DE K.

**Densimetric Estimation of Proteïd.** By THEODOR LOHNSTEIN (*Pflüger's Archiv*, 1895, 59, 479—507).—The estimation of proteïd, especially in urine, by observations on the specific gravity before and after the removal of the proteïd, has been the subject of numerous previous researches. The first part of the present paper is a discussion of these methods, especially that of Huppert and Zahor (*Abstr.*, 1888, 1226). The subject is discussed in its mathematical bearings, and the object aimed at, a constant factor, can be arrived at by employing another substance in solution in addition to the albumin, and observing the sp. gr. after the removal of one and both. The second part of the paper suggests a new densimetric method, and shows that good results are obtained by its use. The proposed method is briefly this: The volume  $v$  of a concentrated solution of sodium hydroxide is brought to the volume  $V$  by dilution with distilled water; the proteïd solution contains  $p$  grams of albumin per 100 c.c.; of this solution a volume equal to  $V$  is taken, and the proteïd precipitated; the coagulum is well washed and dissolved in  $v$  c.c. of undiluted sodium hydroxide, with heat if necessary; this is diluted up to  $V$ . The sp. gr. of the sodium hydroxide solution is noted, and that of the one containing alkali albumin; the two solutions differ by  $\frac{p}{100} V$  gram proteïd.

If  $s_1$  = the sp. gr. of the sodium hydroxide solution, and  $s_2$  that of the sodium hydroxide solution of albumin, then

$$s_2 = s_1 + \beta p,$$

and

$$p = \frac{1}{\beta} (s_2 - s_1).$$

For the method of estimating the coefficient  $1/\beta$  the original paper must be consulted; its mean value is given as 402.45.

W. D. H.

**Analysis of Seeds.** By ERNST SCHULZE (*Chem. Zeit.*, 1894, 18, 799—802).—The author points out the great difficulties connected with the analysis of plants and seeds. The chief part of the paper is, however, devoted to an attack on the process recommended by v. Asbóth (*Abstr.*, 1894, ii, 127), at least when the same is applied to the analysis of seeds.

A sample of vetch seed which, according to v. Asbóth, should have yielded 5.35 per cent. of asparagine and 52.67 per cent. of starch calculated on dry substance, only gave 0.42—0.33 per cent. of asparagine and 36.3 per cent. of starch when tested respectively by Sachsse's and Märcker's processes.

L. DE K.

## General and Physical Chemistry.

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**New Formula for Specific and Molecular Refraction.** By W. F. EDWARDS (*Amer. Chem. J.*, 1894, **16**, 625—634).—Taking the well-known equation for the index of refraction

$$M = \frac{\sin i}{\sin r} = \frac{V}{V_1},$$

where  $V$  is the velocity of light in the ether of space and  $V_1$  is the velocity in the substance, then if  $A$  is the difference between  $V$  and  $V_1$ , we have  $MV - MA = V$  or  $(M - 1)V/M = A$ . If the difference,  $A$ , is proportional to the amount of substance, and if we assume as the unit 1 gram of substance in 1 c.c., and that  $X$  is the retardation of velocity for unit substance,

$$X = \frac{(M - 1)V}{MD};$$

where  $M$  is the index of refraction and  $D$  is the specific gravity of the substance.

If there are several substances in a mixture for which

$$(M - 1)V/MD = C,$$

$C$  being the retardation of  $V$  by the mixture, and  $(m - 1)V/md = a$ ,  $(m_1 - 1)V/m_1d_1 = b$ ,  $(m_2 - 1)V/m_2d_2 = c$ , &c., are the corresponding equations for the components, then  $C = pa + p_1b + p_2c + \&c.$ , where  $p + p_1 + p_2 + \&c. = 1$ , and represent the percentage of the several components of the mixture. Since  $V$  is a factor of both members of the equation, it may be written in the form

$$\frac{(M - 1)}{MD} = \frac{p(m - 1)}{md} + \frac{p_1(m_1 - 1)}{m_1d_1} + \frac{p_2(m_2 - 1)}{m_2d_2} + \&c.$$

Tables are given showing that there is sufficient experimental verification to warrant further work with this formula. H. C.

**Spectrophotometric Researches on Iodine Solutions.** By EDMUND THIELE (*Zeit. physikal. Chem.*, 1895, **16**, 147—155).—In many solutions changes in the absorption coefficients occur on dilution, and are explained by the assumption of dissociation. This explanation is not applicable to solutions of iodine, on which therefore the author undertook spectrophotometric observations, using for the purpose Krüss' apparatus. Solutions in carbon bisulphide, acetic acid, benzene, and paraldehyde were examined. In all, the absorption coefficient falls with dilution, increasing rapidly again, however, with the two latter solvents when a dilution of about 0.0001 is reached. Experiments were next performed to test the constancy of the absorption band. No movement of the band is produced on dilution, although the intensity of the absorption is altered. It appears pro-

able, therefore, that dilution causes no alteration of the molecular weight of the iodine, but that the amplitude of the oscillation is changed.

L. M. J.

**Spectrochemistry of Nitrogen.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 16, 193—225, 226—241).—The atomic refraction of nitrogen was shown by the author (Abstr., 1893, ii, 254) to vary in its different classes of compounds, and he has therefore endeavoured to obtain, as completely as possible, the refractive data of nitrogenous compounds. A spectrometer and a Pulfrich total-reflectometer were employed for the purpose, and with them 132 compounds were examined; the source of each, its treatment, and the physical constants necessary to indicate its purity are given, and a table of the results of the observations is appended. From them, the author draws the following conclusions.

“Saturation isomerides” do not exhibit equal refractive or dispersive powers. In nitro-compounds, the specific refraction and dispersion is less than in the isomeric nitrites, whilst the index of refraction, the boiling point, and the density are greater. The refractive constants of the pyridine derivatives are smaller than those of the aromatic isomerides, the same relation obtaining between the pyrazines and aromatic hydrazines. The triple linkage (C:N) is in its effect on the refractive and dispersive powers equivalent to two double linkages (C=N). A saturated heterocyclic nitrogen compound possesses a higher boiling point, density, and index of refraction, but smaller specific refraction and dispersion than its isomeric olefine derivative.

In the case of “position isomerides” the differences are not so marked. The aldoximes and ketoximes exhibit no differences. In cyclic compounds, those in which the nitrogen is united indirectly to the nucleus have their constants greater than those in which the union is direct. The specific refraction also is greater, the boiling point, density, and index of refraction less, the greater the number of carbon atoms directly united to the nitrogen; the tertiary amines therefore possess the highest constants in a series of isomeric primary, secondary, and tertiary amines.

L. M. J.

**Rotatory Power of Dissolved Substances.** By P. FREUNDLER (*Bull. Soc. Chim.*, 1894, [3], 11, 477—480; compare this vol., i, 174, 210, and 267).—It is becoming more and more evident that solvents which affect the specific rotatory power of a dissolved substance also affect its cryoscopic properties; and that, conversely, when the specific rotatory power of a substance is not affected by the solvent, its cryoscopic properties are normal. The alkylic acidyltartrates and valerates, and certain amylic ethers, afford evidence of the truth of the first part of the statement, whilst fresh evidence in favour of the second part is afforded by isobutylic amylic ether, which gives normal cryoscopic results in benzene solution, and the specific rotatory power of which,  $[\alpha]_D = +1.3^\circ$ , remains practically unaltered by that solvent:  $[\alpha]_D = +1.4^\circ$ . With regard to Ostwald's adverse criticism of the author's cryoscopic observations on benzene solutions, these have been

repeated and extended, with the result of confirming the statement that the values in the cases questioned are below the normal.

The particular question of the connection between polarimetric and cryoscopic anomalies forms part of the broader question of the dependence of the physical properties of solutions on the state of molecular aggregation of the dissolved substance, as illustrated, for example, by Sule's work (*Abstr.*, 1894, ii, 227) on the connection between the polarimetric and ebullioscopic constants of alcoholic and aqueous solutions of rhamnose.

Biot's original generalisation that the specific rotatory power of solutions is independent of the solvent and of concentration, provided there is no chemical action between the active substance and solvent, may still be regarded as true, if it be granted that the apparently anomalous substances either themselves undergo dissociation, or form molecular compounds with the solvent which are capable of dissociation. Aignan and Wyruboff, in particular, have isolated compounds of the latter class; as regards the former class, the alkylic acidyltartrates, the specific rotatory powers of which have been shown to approximate steadily to that of the pure substance as the concentration is increased, may, possibly, undergo a peculiar kind of dissociation into acid anhydrides and derivatives of ethylenic oxide of the

general formula  $\begin{matrix} \text{COOR} \cdot \text{CH} \\ | \\ \text{COOR} \cdot \text{CH} \end{matrix} > \text{O}$ . In support of this hypothesis, it is

to be observed that the benzene solution of methylic diacetyltartrate is acid to litmus, whereas the substance itself is neutral. Should this prove true, it will be possible, by making measurements at two different concentrations, to determine whether the specific rotatory power of a solution is or is not that of the substance itself. JN. W.

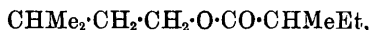
**Ethereal Tartrates.** By PHILLIPE A. GUYE and J. FAYOLLAT (*Compt. rend.*, 1895, **120**, 157—160).—The authors have determined the optical rotation of some ethereal tartrates of the general formula  $\text{C}_2\text{H}_2(\text{OH})(\text{OA})(\text{COOR})_2$ , where A is some acid radicle. Their results are given in the following table.

	$[\alpha]_D$		$[\alpha]_D$
Ethyl tartrate .....	+ 5.25	Isobutyl tartrate .....	+ 11.8
„ monoacetyltartrate ...	+ 2.4	„ monoacetyltartrate .	+ 7.8
„ monopropionyltartrate	+ 2.3	„ monobutyryltartrate	+ 9.7
„ monobutyryltartrate ..	+ 1.8	„ monobenzoyltartrate	+ 11.5
„ monobenzoyltartrate ..	+ 1.5		

These results are shown to be in accordance with Guye's general theory of the rotatory power of homologous substances (*Abstr.*, 1893, ii, 561). H. C.

**Superposition of the Optical Effects of different Asymmetrical Carbon Atoms in the same active Molecule.** By PHILLIPE A. GUYE and M. GAUTIER (*Compt. rend.*, 1894, **119**, 953—955).—The authors have previously shown (this vol., ii, 149) that the two similarly asymmetrical carbon atoms in amylic ether each act on polarised light as if the remainder of the molecule were inactive,

the observed effect being the algebraic sum of their separate effects. Experiments with amylic valerate and amylic amylglycollate show that this is also true when the two asymmetrical carbon atoms are associated with dissimilar instead of similar groupings. According to this view, the optical rotation caused by the amylic valerate (1)  $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CHMeEt}$  should be approximately equal to the sum of the rotations produced by the amylic valerate (2)



in which there is only one asymmetrical carbon atom (in the valeric acid), and the valerate (3)  $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , in which there is also only one asymmetrical carbon atom, belonging, however, to the amyl radicle.

The third compound has recently been described (this vol., i, 202); a column 500 mm. long has a rotatory power =  $+1.08^\circ$ . The second salt is obtained by the interaction of active valeric acid and inactive isoamylic alcohol; its rotatory power for a column 500 mm. long is  $+4.26^\circ$ . The sum of the two values is  $+5.34^\circ$ .

Amylic valerate was prepared by the interaction of active valeric acid and racemised amylic alcohol, and also by the interaction of racemised valeric acid and active amylic alcohol; the rotation of the first product was  $+4.40^\circ$  and of the second  $+1.22^\circ$ . The ethereal salts thus obtained are mixtures of two salts which cannot be separated by fractional distillation, but it is clear that they should behave towards polarised light as if the effect of one of the asymmetrical carbon atoms was neutralised in the first case, and the effect of the other in the second case. The sum of the two observed rotations is  $+5.62^\circ$ .

The amylic valerate (1) was prepared by the interaction of active valeric acid and active amylic alcohol; its rotatory power in a column 500 mm. long is  $+5.32^\circ$ , and this agrees fairly well with the two values  $+5.34^\circ$  and  $+5.62^\circ$  obtained by the indirect methods.

The results obtained with amylic amylglycollate will be described subsequently.

C. H. B.

**Magnetic Rotation of Solutions of Hydrogen Chloride.** By OTTO SCHÖNROCK (*Zeit. physikal. Chem.*, 1895, 16, 29—44).—The magnetic rotation of hydrogen chloride in aqueous solution, according to the observations of Perkin (*Trans.*, 1889, 680; 1894, 20), is double that of its solution in isoamylic ether, and the cause has been ascribed to the electrolytic dissociation in the former solvent. The author had previously found an equal rotation in the two solvents (*Abstr.*, 1893, ii, 443), and has therefore carefully repeated and extended his researches. Solutions of the gas in water, isoamylic ether, isoamylic alcohol, ethylic alcohol, and in mixtures of these compounds were examined. The rotations of the solvents were first obtained and then those of the solution, 25 liquids being so treated. The rotation is taken from the mean of four or five separate results, and is given in thousandths of a minute.\*

\* An unnecessary refinement, however, as the separate results under similar conditions differ in many cases by nearly a minute.

The results may be summarised by a table; values due to Perkin being added and marked \*; the first column for each solvent giving concentration, the second the molecular rotation.

Water.		Amylic ether.		Amylic alcohol.		Ethylic alcohol.	
11·45	4·774	0·76	4·036	1·58	5·413	6·59	4·491
25·06	4·404	2·34	2·838	6·89	4·028	9·78	4·201
*15·63	4·419	3·45	3·322	9·49	3·809	14·64	4·232
*25·60	4·405	8·96	2·101	*25·45	3·285	*40·04	3·365

The rotation decreases with increasing concentration not only in aqueous solutions, but in those of other solvents; hence the author considers that dissociation has no effect on the magnetic rotation of solutions.

L. M. J.

**Electrical Potentials in a Liquid Conductor in Uniform Movement.** By G. GOURÉ DE VILLEMONTÉE (*Compt. rend.*, 1894, 119, 1201, 1202).—Mercury, and solutions of zinc, copper, and nickel sulphates containing 10 grams of the salt per litre, were caused to move through insulated horizontal or vertical glass tubes, of uniform bore, the diameter being 3 mm. for mercury and 8 mm. for the saline solutions, and observations were made with a view to detect differences of potential between two points in the liquid. The capillary electrometer used would indicate a difference of 0·00015 volt. The electrodes consisted of platinum wires, the ends of which were coated with an electrolytic deposit of the metal contained in the saline solution. Sometimes both electrodes were in the path of the moving liquid, sometimes one was in the moving liquid and the other in the reservoir. The rate of movement of the liquids was 33·5 mm. per second in the horizontal tubes and 155·3 to 323 mm. in the vertical tubes.

The results show that the uniform movement of a liquid conductor along wide insulated glass tubes of uniform section produces no appreciable difference of potential between two points in the liquid within the limits of velocity specified.

C. H. B.

**Measurement of the Specific Inductive Capacities of Water, Alcohol, &c.** By REGINALD A. FESSENDEN (*Phil. Mag.*, 1894, [5], 38, 567—568).—It has hitherto been accepted that the high values for the specific inductive capacities for water, alcohol, and some other similar liquids which have been obtained by various experimenters are correct. If this were so, Maxwell's rule for the relation between specific inductive capacity and the index of refraction would not hold in these cases, and the phenomena of dispersion, &c., have been called in to explain this anomaly. The author finds, however, from the results of experiments described in the paper, that these high values are not correct, but that the true values are in every one of these substances very nearly equal to those called for by the theory.

The cause of the errors lies in the fact that electrolysis gives a



capacity effect. It is for this reason that Kohlrausch's method almost always gives erroneous results, as what is measured is not the resistance of the electrolyte, but its impedance. H. C.

**Thermodynamics of Galvanic Polarisation.** By HANS JAHN and OTTO SCHÖNROCK (*Zeit. physikal. Chem.*, 1895, **16**, 45—71).—The authors develop, from the thermodynamical standpoint, formulæ for the cathodic, anodic and total polarisation for a solution. From these it is indicated that if the potential difference between a metal and its solution be subtracted from the total polarisation, the difference should be constant in the case of the strong oxy-acids, a result agreeing with experimental data. The E.M.F.s of various chains are also calculated and compared with the found results. Under similar conditions, all oxy-acids should show the same potential difference at the commencement of the gas development, a result experimentally obtained by Le Blanc. The polarisation should be independent of the concentration, and experiments with sulphuric acid gave the following results: normal solution 2.3977 volts, decinormal solution 2.3922. The nature of the electrode affects the polarisation; the size, however, should not affect the final value. In the case of salt solutions, similar laws obtain, the polarisation increasing with the polarising E.M.F. and being independent of the concentration. The polarisation of dilute solutions of bases should be equal to that of dilute acids, and this conclusion is verified by experiments with solutions of potassium and sodium hydroxides, ammonia, ethylamine, and diethylamine. L. M. J.

**Rôle of Atomic Heat in the Periodic Series of the Elements.** By CHARLES T. BLANSHARD (*Phil. Mag.*, 1895, [5], **39**, 106—115).—The author sets forth a number of relationships deduced from a study of the latest and most accurate data for atomic heats and melting points. The atomic heat is found to decrease in any series from the monad to the tetrad element, and then increases till a maximum is reached with the heptad element. The variation is greatest with elements of low atomic weights, becoming less and less as the atomic weight increases. In Groups I and II (the metallic groups), as the atomic weight increases, both the melting point and the atomic heat decrease. In Groups III and IV (intermediate groups), as in all the sub-groups of the periodic system, the atomic heat increases with the atomic weight, whilst the melting point decreases: the former being characteristic of the non-metals, the latter of the metals. In Groups V, VI, and VII (non-metallic groups), as the atomic weight increases so do both atomic heat and melting point. In Group VIII, the melting point increases with the atomic weight, whilst the atomic heat decreases: the former being a non-metallic, the latter a metallic characteristic.

A table is also given of the volume heats (= atomic heat ÷ atomic volume) of the elements, the specific gravities being taken at 0° and the specific heats as near 15° as possible. In each natural group of elements, volume heat varies inversely as atomic volume. The variations become less and less as the valency for oxygen rises, until the seventh group is reached, when it becomes constant. As atomic heat

increases in some groups and decreases in others with increase of atomic weight, whilst atomic volume regularly increases, it is evident that the increase in atomic volume proceeds at a higher ratio than the variation in atomic heat. Atomic weight being a constant increment, it follows from the above that in any natural group specific gravity varies more than specific heat.

H. C.

**Specific Heat of Metallic Tungsten.** By A. W. GRODSPEED and EDGAR F. SMITH (*Zeit. anorg. Chem.*, 1895, **8**, 207—212).—The method employed by the authors is that described by J. Joly (*Roy. Soc. Proc.*, 1886, **41**, 248 and 352). Full details are given in the original paper. The mean of the results obtained is specific heat = 0.03380, with a probable error of  $\pm 0.0003$ . When this number is multiplied by the value for the atomic weight of tungsten obtained by Smith and Pennington (this vol., ii, 230), we get  $184.921 \times 0.0338 = 6.25$ , and, taking the value obtained by Smith and Desi (this vol., ii, 231),  $184.704 \times 0.0338 = 6.243$ .

E. C. R.

**Specific Heats of Gases.** By H. PETRINI (*Zeit. physikal. Chem.*, 1895, **16**, 97—117).—The difference between the capacities for heat at constant pressure and at constant volume for gram molecules of the gas is nearly equal to 2 ( $C_p - C_v = 1.98$ ). If the ratio of the specific heats  $c_p/c_v$  is given by the expression  $1 + \frac{2}{2n+1}$ , where  $n$  is the number of atoms in the molecule, we obtain the results  $C_v = (2n+1) \times 0.99$ ,  $c_v = C_v/A$ , and  $c_p = c_v + 1.98/A$ , where  $A$  = the molecular weight of the gas. A very complete table of the known gaseous specific heats is given, with the results as calculated above. In general, the law  $c_p/c_v = 1 + \frac{2}{2n+1}$  is seen to hold.

The chief exceptions are carbon bisulphide and sulphurous anhydride (in which the calculated value for  $c_p/c_v$  is too small), ammonia, methane, and ethylene (where this ratio is too great), and compounds which contain more than one atom of a halogen. The author considers that the exception in the case of carbon bisulphide may be ascribed to polymerisation, and in the halogen compounds to dissociation. The influence of temperature on the specific heat is considered; a marked increase in  $c_p$ , occurring with rise of temperature in the case of ammonia, methane, and ethylene. An expression for the dissociation is also obtained, and compared with experimental data.

L. M. J.

**Influence of Temperature on the Specific Heat of Aniline.** By ERNEST H. GRIFFITHS (*Phil. Mag.*, 1895, [5], **39**, 47—77 and 143—144).—In addition to the fact that our knowledge of its capacity for heat at different temperatures is far from satisfactory, water is, for other reasons, by no means an ideal standard for calorimetry. Its capacity for heat is so great that the changes in temperature caused by the immersion in it of bodies whose specific heats are small are too minute to be measured with exactness under ordinary circumstances. What is required is a liquid of small capacity for heat, whose temperature coefficient of specific heat is accurately known, easily obtain-

able in a fairly pure state, and having a low vapour pressure at ordinary temperatures. The author believes that aniline is a liquid fulfilling these conditions, and, in order to furnish data necessary for its successful use, has determined its specific heat over a range of  $15^{\circ}$  to  $52^{\circ}$ .

The method adopted, of which all necessary details are given in the paper, was to supply heat to the interior of the calorimeter by means of an immersed conductor, whose ends were kept at a constant potential difference. The following formula gives the specific heat curve between the limits of temperature already named.

$$S_1 = 0.5156 + (\theta_1 - 20) \times 0.0004 + (\theta_1 - 20)^2 \times 0.000002.$$

The following table gives the experimental results and those obtained from the above formula.

$\theta_1$ .	$S_1$ obs.	$S_1$ cal.
$15^{\circ}$ .....	0.5137 .....	0.5137
20 .....	0.5155 .....	0.5156
25 .....	0.5175 .....	0.5176
30 .....	0.5198 .....	0.5198
35 .....	0.5221 .....	0.5221
40 .....	0.5244 .....	0.5244
45 .....	0.5268 .....	0.5269
50 .....	0.5294 .....	0.5294
52 .....	0.5304 .....	0.5305

H. C.

### Critical Temperature as a Test of the Purity of Liquids.

By RAOUL PICTET and MICHAEL ALTSCHUL (*Zeit. physikal. Chem.*, 1895, **16**, 26—28, and *Compt. rend.*, 1895, **120**, 43—46).—The critical point of a liquid is altered to a much greater extent than the boiling point by the presence of impurities, and hence the direct determination of the critical temperature affords a valuable indication as to the purity of the liquid.

The liquid is placed in a glass tube about 50 mm. long and 3 mm. internal diameter, with walls about 1 mm. thick, and is then boiled to expel all traces of air, the tube being hermetically sealed. It should be about one-third full of liquid, and the remainder is, of course, filled with saturated vapour. These tubes are then heated in a jacket consisting of two concentric cylinders of wire gauze, with two windows of mica to allow of the examination of the tube. There is an outer layer of asbestos, and below the cylinders are several sheets of wire gauze to distribute uniformly the current of hot air from the burner. A thermometer is fastened to the glass tube. The temperature is observed when the meniscus disappears, or when the characteristic mist forms in the tube.

Quantities of alcohol in chloroform or ethylic chloride, or of acetaldehyde in valeraldehyde, alter the critical temperature by  $1.7^{\circ}$  to  $6.0^{\circ}$ , whilst the corresponding alterations in the boiling points are only  $0.1^{\circ}$  to  $0.6^{\circ}$ .

The change in the critical temperature is always in the same direction as the change in the boiling point. Ethylic alcohol reduces the

boiling point and critical temperature of chloroform, but raises the boiling point and critical temperature of ethylic chloride.

C. H. B.

### Critical Temperature of Liquids holding Solids in Solution.

By RAOUL PICTET (*Compt. rend.*, 1895, 120, 64—67).—The observations were made in the manner previously described (preceding abstract). Ether was mixed with borneol, cineol, terpineol, phenol, guaiacol, and iodine, in the proportion, as a rule, of 1 part of the solid to 50 parts of ether.

With 0.5 gram of borneol and 25 grams of ether, the boiling point is raised by  $0.2^{\circ}$ , but the critical point by  $8^{\circ}$ , the critical temperature of the solution being  $197^{\circ}$ . At this point, the meniscus completely disappears, but there is no deposit of borneol, which remains gaseous in the ether vapour, although its melting point is  $198^{\circ}$ . At the ordinary pressure, borneol is not volatile in ether vapour. Even with 45 grams of borneol and 55 grams of ether, the critical point being  $296^{\circ}$ , the whole of the borneol remains at this temperature dissolved in the ether vapour.

A precisely similar result is obtained with borneol and ethylic chloride, the critical temperature being  $181^{\circ}$ , and with ether and guaiacol, iodine, or phenol. In all cases there is a rise in the boiling point of  $0.1^{\circ}$  to  $0.3^{\circ}$ , but a rise in the critical temperature of  $4^{\circ}$  to  $12^{\circ}$ .

A solution of alizarin in ethylic alcohol shows the same phenomenon; at the critical temperature,  $240^{\circ}$ , the alizarin remains completely dissolved in the alcohol vapour, although the temperature is  $50^{\circ}$  below its melting point ( $290^{\circ}$ ).

In 1877 the author suggested that the liquefaction of vapour takes place in two distinct phases: one at temperatures above the critical point, in a number of points in the midst of the vapour, the number being proportional to the pressure; the other below the critical point, under the pressure of the saturated vapour. Only in the second case does gravity intervene and produce permanent drops. In the first case, the existence of the vesicle is so brief that it evaporates almost as soon as it is formed, and is replaced by another in its immediate neighbourhood. These small, liquid spheres never form a drop or a meniscus visible to the eye; permanent liquefaction can, in fact, only take place below the critical temperature. Adopting this view, it is clear that solid bodies might dissolve in the aggregate of liquid vesicles suspended in the same vapour under high pressure and near the critical temperature. If this explanation is correct, it follows that the solids will be deposited if the vapour is superheated, owing to the rapid volatilisation of the vesicles. Should no such deposition take place, it will follow that, contrary to all laws concerning changes of state, solid bodies can become gaseous and mix with other gases at temperatures much below their melting points, and under considerable pressures from their own vapours.

C. H. B.

*Note by Abstractor.*—The fact that many solids dissolved in liquids remain dissolved or diffused in the vapours of the liquids at, and even above, the critical temperature of the latter, although this tempera-

ture may be below the melting point of the solid, was observed by J. B. Hannay and J. Hogarth in 1880 (Abstr., 1880, 210—211 and 693), and they state that, in the case of potassium iodide and alcohol, no deposition of the solid occurs at temperatures much above the critical point. Ramsay was unable to confirm this result with potassium iodide in alcohol. Hannay and Hogarth state (*loc. cit.*) that when a red-hot iron is brought near one side of the tube containing the gaseous solution, there is deposition of the solid on that part of the tube which is thus heated, but the deposit redissolves when the local disturbance of temperature is removed. This would seem to confirm Pictet's explanation. (See also Hannay and Hogarth, *Roy. Soc. Proc.*, **30**, 178—188 and 484—490, and W. Ramsay, *ibid.*, **30**, 323—329, and **31**, 194—206.) C. H. B.

**Heat of Combination of Water of Crystallisation of Organic Compounds.** By W. J. JORISSEN and E. VAN DE STADT (*J. pr. Chem.*, 1895, [2], **51**, 102—106).—The heat of combination of liquid water with the solid substance to form the solid hydrate can be determined for organic substances which contain water of crystallisation in three ways: from the vapour tension, from the heat of solution, and from the heat of combustion. The authors have compared the numbers obtained by the last two of these methods for a series of compounds, the data being partly taken from previous determinations and partly from their own experiments, and have found on the whole a satisfactory agreement.

	From heat of solution.	From heat of combustion.
Citric acid ( $1H_2O$ ) . . . . .	2·61	3·2
Racemic acid ( $1H_2O$ ) . . . .	1·48	(1·2)
Creatine ( $1H_2O$ ) . . . . .	3·5	6·7
Milk sugar ( $1H_2O$ ) . . . . .	6·16	6·2
Oxalic acid ( $2H_2O$ ) . . . . .	6·3	7·4
Raffinose ( $5H_2O$ ) . . . . .	17·9	6·8

A. H.

**Thermal Properties of Nitrobenzoic acids.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1894, [3], **11**, 560—562).—The heats of dissolution of these acids, calculated from the heats of dissolution in aqueous soda, are for the ortho-acid, +9·45 Cal.; for the meta-acid, +7·15 Cal.; and, for the para-acid, +6·20 Cal. The heats of dissolution of the anhydrous sodium salts are +0·31 Cal., —1·03 Cal., and —1·90 Cal. respectively. The heats of formation of these salts, calculated from the above data, are +20·39 Cal., +19·39 Cal., and +19·31 Cal. respectively. The heat of formation of sodium benzoate being +17·4 Cal., it follows that the augmentation of the heat of formation caused by the nitro-group diminishes with its distance from the carboxyl, a result similar to that obtained with the phthalates. Comparing the heats of formation of sodium benzoate, +17·4 Cal.; salicylate, +19·15 Cal.; orthonitrobenzoate, +20·39 Cal.; and phthalate, +22·12 × 2 Cal., it is seen that carboxyl is more negative than the nitro-group, and this, in turn, than the hydroxyl group. JN. W.

**Influence of the Relative Volumes of Liquid and Vapour on the Vapour Pressure of a Liquid at Constant Temperature.**

By SYDNEY YOUNG (*Phil. Mag.*, 1894, [5], 38, 569—572).—It has been stated by Batelli that when, in a tube containing a perfectly pure liquid and its vapour, the volume is diminished and the vapour caused to condense, the vapour pressure rises; in other words, that the smaller the relative volume of vapour, the higher is the vapour pressure. The author has recently been engaged in determining the vapour pressures of isopentane (b. p.  $28^{\circ}$ ) at various temperatures, and in many cases the volumes of liquid and vapour were read. The results, some of which are given in full in the paper, prove conclusively that the vapour pressures of isopentane are independent of the relative volumes of liquid and vapour.

If, however, a trace of air happens to have entered the tube, or to have been left in the liquid, or a small quantity of permanent gas has been formed by partial decomposition of the liquid by prolonged heating at high temperatures, the presence of permanent gas (or of very volatile impurity) is clearly indicated by the increase of pressure required for the complete condensation of the vapour. The following points have been noticed in such cases:—(1) The pressure does rise as the volume of vapour diminishes; (2) the readings taken with diminishing volumes are higher than with increasing volumes.

H. C.

**The Relation between Dissociation and Temperature.** By HANS JAHN and E. SCHRÖDER (*Zeit. physikal. Chem.*, 1895, 16, 72—90).—Determinations were made by Kohlrausch's method of the conductivity of aqueous solutions of formic, acetic, propionic, butyric, isobutyric, and valeric acids. Each acid was employed in  $\frac{1}{16}$ ,  $\frac{1}{32}$ ,  $\frac{1}{64}$ ,  $\frac{1}{128}$  normal solutions, and at a series of temperatures varying from  $10^{\circ}$  to  $50^{\circ}$ . The results at each concentration are expressed by an interpolation formula\* which in all cases satisfactorily reproduces the observed numbers. The conductivity at infinite dilution is calculated from determinations with the sodium salts by the expression  $\lambda_{\infty} = \lambda_{\text{HCl}} - \lambda_{\text{NaCl}} + \lambda_{\text{NaR}}$ , and a temperature formula given. The constant  $(\lambda_v/\lambda_{\infty})^2/(1 - \lambda_v/\lambda_{\infty})$  is obtained at temperatures  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ , and  $40^{\circ}$ . The values are approximately constant, except for the higher concentrations, and vary but slightly with the temperature, so that the increase of conductivity with temperature appears to be chiefly due to the decrease of the ion friction. The heat of dissociation is also calculated for each of the first five acids at each dilution, the values being recorded in a table. They are in all cases negative and, as might be expected, very small.

L. M. J.

**Certain Regularities in the Weights of Drops of Molten Metals.** By ISIDORE TRAUBE (*Ber.*, 1895, 28, 419).—Remarks on Thaddéeff's paper on this subject (this vol., ii, 161). C. F. B.

\* It appears noticeable that with each acid the interpolation formulæ are in all cases of the form  $\lambda = a + bt - ct^2$ , so that a maximum should occur at the temperature  $b/2c$  if the expression were applicable to higher temperatures. This is in most of the experimental series about  $80^{\circ}$  to  $120^{\circ}$ , and at infinite dilution about  $150^{\circ}$  to  $170^{\circ}$ .

**Volume Change on Neutralisation.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1895, **16**, 91—96 and 139—146).—In the first paper, the volume changes on neutralisation are recorded in the cases of a dilute solution of sodium hydroxide with hydrochloric, sulphuric, acetic, and monochloroacetic acids. The determinations were made by the method of density observations with Sprengel's pyknometers. With the strong, completely dissociated acids, hydrochloric and nitric, the volume change alters but slightly with concentration—about 20 per cent. from 1.0 to 0.005 normal solutions. With sulphuric acid, the increase was about 90 per cent.; with monochloroacetic acid 60 per cent., and with acetic acid 50 per cent.

In the second paper, the author endeavours to prove that the volume alteration is due to the effect of the altered internal pressure, and may be calculated from the compressibility coefficient and the change in internal pressure. Amagat's results supplying compressibility data, the author calculates the volume change at 20° in the case of the neutralisation of sodium and potassium hydroxides by hydrochloric acid, the calculated and observed results showing satisfactory agreement. Expressing the volume change in terms of the differences in internal pressure by an equation,

$$\Delta v = \mu \times 10^{-7} V \left[ \frac{1}{2} (\Delta k_a + \Delta k_b) - \Delta k_s \right];$$

if the volume is  $V$ , the reciprocal of the concentration, then the product  $V\Delta k$  should be independent of the concentration, and  $\Delta v$  should vary as  $\mu$ . This is found to be the case by experiments with sodium hydroxide and hydrochloric acid. Similarly  $\Delta v$  should vary with the temperature in the same manner as  $\mu$ , where  $\Delta k$  is independent of the temperature. In the case of water,  $\mu$  decreases between 0° and 50° by about 14 per cent., increasing above this temperature. In 1/1000 solution of the above compounds,  $\Delta v$  changes from 20.9 at 0° to 18.7 at 30°, and from 100° to 140° increases 37 per cent., while  $\mu$  between the same temperature increases 30 per cent. The calculated volume change, owing to decomposition of a binary electrolyte into its ions, is calculated as 9—10 c.c., the observed value for various electrolytes varying from 8 to 12 c.c. (gram equivalent per litre). L. M. J.

**The Freezing Point of Liquid Mixtures.** By RAOUL PICTET and MICHAEL ALTSCHUL (*Zeit. physikal. Chem.*, 1895, **16**, 18—23).—Two sets of aqueous solutions of alcohol were prepared, the first containing 1, 2, 3, &c., mols. of water per mol. of alcohol, the second containing 1, 2, 3, &c., per cent. of water. The results of the freezing point determinations are expressed by curves. The second curve is approximately a hyperbola; the first shows numerous breaks, and is made up of a number of straight lines with irregular joining portions. Some of these straight lines pass through the origin, but others do not; for example, the portions between 16.4 and 30 per cent., and between 39 and 65 per cent. The author hence considers that here the lowering is proportional to the quantity of some dissolved hydrate. A table is added of the freezing points from  $C_2H_5O + 100OH_2$  (−1.0°) to  $C_2H_5O + OH_2$  (−51.3°). L. M. J.

**Maximum Depression of the Freezing Point of Mixtures.**

By EMANUELE PATERNÒ and CLEMENTE MONTEMARTINI (*Gazzetta*, 24, ii, 208—222).—The authors have made a number of experiments on the depression of the freezing point of solvents by dissolved substances, using solutions containing from 0—10 per cent. of dissolved matter. It might be expected that the maximum depression of the freezing point of mixtures of two liquids would be obtained when the two substances were present in some simple molecular proportion. This was found to be the case in the several instances investigated; mixtures in the ratio of 1 mol. of paraxylene with 2 mols. of acetic acid, 1 of paraxylene with 2 of phenol or 3 of trimethylcarbinol, and 6 of phenol with 1 or 2 of trimethylcarbinol, have lower freezing points than any other mixtures of the two constituents. The maximum depression of the freezing point of paraxylene by benzene is obtained when about 1 mol. of each is present.

W. J. P.

**Cryoscopic Behaviour of Substances having Constitutions similar to that of the Solvent.** By FELICE GARELLI and C. MONTANARI (*Gazzetta*, 24, ii, 229—263).—Garelli (*Abstr.*, 1894, i, 157) has shown that, in determining the molecular weight of a substance by the cryoscopic method, anomalous results are obtained if the solvent has a constitution similar to that of the substance dissolved; the cause of this behaviour was assigned to the formation of a solid solution of the two components, a view which is amply justified by the present series of cryoscopic determinations with a large number of pairs of substances.

Diphenylene oxide and coumarone, both of which contain the furfuranic nucleus, cause slightly anomalous depressions of the freezing points of phenanthrene and naphthalene respectively; the irregularity diminishes in degree as the number of benzenoid radicles present in the furfurane nucleus decreases, so that pyromucic acid depresses the freezing point of benzoic acid normally.  $\beta$ -Naphthaquinoline gives too high a molecular weight in phenanthrene, whilst phenanthroline gives the normal depression. Molecular weight determinations of toluene and isomethyleugenol in benzene solution show that the introduction of an aliphatic side chain into the benzene nucleus alters the configuration of the molecule to such an extent that normal results are obtained in benzene solution; such is not the case with phenols and aromatic amides, the molecular configuration of benzene is so slightly altered by the introduction of an hydroxyl or amidogen group that solid solutions are still obtained. Quinol is the only dihydroxybenzene which gives the theoretical depression in phenol solution, the depressions caused by its isomerides being too small.

Benzoic acid solutions of naphthalene, acetanilide, diphenylamine, resorcinol, and thymol were examined in order to determine the molecular depression of the freezing point; this was found to be 78.5. 2-Thiophenic, 2-pyrrolinecarboxylic, salicylic, and metahydroxybenzoic acids give high molecular weights in freezing benzoic acid, whilst pyromucic, parahydroxybenzoic, and the three amido-benzoic acids give almost normal values, the para-compounds being the most satisfactory in this respect. The behaviour of benzamide



in benzoic acid solution is quite normal, so that the power of forming solid solutions is lost by the substitution in the side chain.

The molecular depression of the freezing point of acetophenone was found to be 56.4, from determinations made with naphthalene, nitrobenzene, bromobenzene, aniline, acetone, and salicylic and benzoic acids; this number differs considerably from 74.4, the constant deduced from Raoult's law. 2-Acetylpyrroline, 1-acetylpyrroline, and acetothienone, which have constitutions somewhat similar to that of acetophenone, form solid solutions with it.

The molecular depression of the freezing point of succinic anhydride was found to be 63 from determinations made with isoapiole, acetanilide, and succinimide. With this solvent, maleic anhydride forms isomorphous mixtures the melting points of which can be calculated by Küster's rule. Oleic and palmitic acids give normal molecular weights in stearic acid solution.

The depression of the freezing point of crotonic acid by isocrotonic acid is normal, as would be expected from the dissimilarity in constitution of these two substances. Metanicotine is found to depress the freezing point of diphenyl normally, a result which favours the constitution assigned to the base by Pinner (Abstr., 1893, i, 736).

W. J. P.

**The Freezing Points of Isomorphous Mixtures.** By FELICE GABELLI (*Gazzetta*, 24, ii, 263—274).—Küster has shown (Abstr., 1894, ii, 274) that if the composition of the solid matter which separates on cooling a melted mixture of two substances is the same as that of the liquid above it, the melting point of the mixture can be directly calculated from those of the components. The author now shows, in the case of mixtures of anthracene with phenanthrene, of carbazole with phenanthrene, and of carbazole with anthracene, that although the melting points of the mixtures are limited by those of their components, yet considerable differences exist between the melting points observed and those calculated by Küster's rule. No explanation of the anomalous behaviour of such mixtures is given by van't Hoff's theory of solid solutions.

W. J. P.

**Reduction of the Freezing Point of Dilute Solutions of Sodium Chloride.** By A. PONSOT (*Compt. rend.*, 1895, 120, 317—319).—With the aid of the apparatus described in a former paper (Abstr., 1894, ii, 342), the author has determined the freezing points of dilute solutions of sodium chloride. For temperatures from 0° to -1.5°, a thermometer was used graduated to  $\frac{1}{100000}^{\circ}$ , and for temperatures from -0.5° to -4° a thermometer graduated to  $\frac{1}{1000}^{\circ}$ . The molecular reductions are calculated, and the results compared with those of Jones, Arrhenius, Loomis, and Pickering. The values obtained for the molecular reductions are throughout lower than those of the other observers, and the reduction is proportional to the weight of salt contained in 100 grams of the solvent. Similar results were obtained with potassium chloride solutions.

H. C.

**The Freezing Points of some Organic Liquids.** By MICHAEL ALTSCHUL and B. V. SCHNEIDER (*Zeit. physikal. Chem.*, 1895, 16,

24—25).—The authors have determined the freezing points of some organic liquids which only solidify at low temperatures. Their results gave:—Benzic chloride,  $-47.9^{\circ}$ ; benzylidene chloride,  $-17.0^{\circ}$ ; benzo-trichloride,  $-17.0^{\circ}$ ; benzaldehyde,  $-13.5^{\circ}$ ; piperidine,  $-17^{\circ}$ ; quinoline,  $-19.5^{\circ}$ ; cinnamaldehyde,  $-7.5^{\circ}$ ; propionic acid,  $-24.5^{\circ}$ ; orthoxylene,  $-45.0^{\circ}$ . The other liquids examined did not freeze at  $-100^{\circ}$  or  $-80^{\circ}$ . From these results, the authors consider that addition of a methyl group in the benzene nucleus lowers the freezing point, which is, however, raised by the substitution of chlorine for hydrogen, and that in isomeric compounds the iso-compound has the lower freezing point.

L. M. J.

**Paraxylene as the Solvent in Cryoscopic Investigations.** By EMANUELE PATERNÒ and CLEMENTE MONTEMARTINI (*Gazzetta*, 24, ii, 197—208).—The high freezing point of paraxylene ( $16^{\circ}$ ) would recommend it as a solvent in cryoscopic determinations; the authors have therefore made a number of trials with this hydrocarbon in order to ascertain its suitability for this purpose. The depressions of the freezing point of paraxylene by 24 hydrocarbons, organic salts, alkaloids, alcohols, acids, and phenols were determined; the molecular depression, as calculated from the experiments with benzene, naphthalene, diphenyl, ethylic oxalate, thiophen, aniline, and tribenzylamine is 43.34. The constant calculated from Colson's determination of the latent heat of fusion is 42.5, and may be taken as 43 for practical purposes.

Paraxylene, when used as a solvent for cryoscopic determinations, behaves very similarly to benzene; normal molecular weights are obtained with hydrocarbons, ethers, anhydrides, alkaloids, and neutral substances generally, whilst alcohols and phenols depress the freezing point abnormally, just as they do that of benzene.

W. J. P.

**Solubility Experiments.** By ARTHUR A. NOYES and CHARLES G. ABBOT (*Zeit. physikal. Chem.*, 1895, 16, 125—138).—When, to a saturated solution of a salt, a second salt containing one similar ion is added, the quantities of the dissolved compounds is calculable on the assumption that (i) the quantity of dissolved undissociated salt remains unchanged, and (ii) the product of the quantities of the two ions is still the same. The values obtained by experiment and calculation, however, have, as a rule, shown only approximate agreement, and doubts have been thrown on the validity of the above solubility laws (Abstr., 1893, ii, 364). The authors have therefore tested the law by a series of experiments on the solubility of the chloride, bromate, and thiocyanate of thallium. The salts were all prepared from the pure metal, and great pains taken to ensure their perfect purity. The solubility of each salt in water was determined, the three pairs of saturated solutions mixed, and the quantity of each salt in solution estimated. Then if  $m_0$ ,  $m_0'$ ,  $m$ , and  $m'$  are solubilities of the two salts in the water and mixed solution, and  $a_0$ ,  $a_0'$ ,  $a$ ,  $a'$  their degree of dissociation, the equations obtain  $m_0(1 - a_0) = m(1 - a)$ ; (2)  $m_0'(1 - a_0') = m'(1 - a')$ ; (3)  $m_0^2 a_0^2 = ma(ma + m'a')$ ;  $m_0'^2 a_0'^2 = m'a'(m'a' + ma)$ . From these the constants  $a_0$  are calculable. The value  $a_0$  for each salt is thus obtained from two independent experiments, and

the agreement of the values forms the test of the validity of the law. The results gave for  $100a_0$ :—thallium chloride, (1) 86·5, (2) 86·5; thallium thiocyanate, (1) 86·7, (2) 86·6; thallium bromate, (1) 89·9, (2) 91·1. The values, as calculated from conductivity experiments, were 86·6, 85·6, and 89·0. The solubility influence law is therefore, the authors consider, undoubtedly valid.

L. M. J.

**Some Properties of Calcium Chloride Solutions. Part I, Freezing Points; Part II, Heat of Dissolution; Part III, Densities, and Discussion of the Results.** By SPENCER U. PICKERING (*Ber.*, 1893, 26, 2766—2771; 1894, 27, 67—75, 1379—1385).—The solutions examined ranged from a strength corresponding with the hexahydrate down to the weakest solutions possible. The results were examined critically with a view of ascertaining whether they all indicated changes of curvature at the same points. This was found to be the case, and drawings which showed these changes agreed well with the ascertained experimental error; whereas drawings obliterating these changes, or placing changes at other points, were found not to do so. The hydrates which were indicated as existing by all three properties were those with about 10, 13, 17, 29, and 1500  $H_2O$ , but from the magnitude of the experimental error as compared with the smallness of the difference in strength corresponding with an additional molecule of water, it was impossible to say whether the changes occurred at simple molecular proportions or not. In all cases where changes were not indicated by all the properties alike, the evident cause was absence of sufficient experimental data in some of the series. The freezing points were extended somewhat beyond the strength corresponding with  $CaCl_2 \cdot 6H_2O$ , and in this region either this hydrate or two distinct forms of a tetrahydrate may be made to crystallise from the same solution. The molecular depression of the freezing point of the hexahydrate by water is only  $0.003^\circ$  for  $H_2O$  to  $100(CaCl_2 \cdot 6H_2O)$ , which is about one-seventieth of that given by van't Hoff's equation; it increases rapidly to  $0.099^\circ$  as the proportion of water present is increased.

S. U. P.

**A New Method for the Determination of Isosmotic Concentrations.** By H. KÖPPE (*Zeit. physikal. Chem.*, 16, 261—288).—A small graduated pipette with a funnel-shaped end is partially filled with blood, and the volume noted. A salt solution is then introduced and the liquids mixed, after which the ends are closed and the pipette placed in a centrifugal machine, by which means the corpuscles collect at the end of the pipette, and their volume is determined. Other circumstances being similar, namely, quality of blood, centrifugal force, &c., the ratio of the volume of the blood corpuscles to that of the blood itself depends on the osmotic pressure of the solution, decreasing as the osmotic pressure rises; it can hence be used as a measure of this constant. In all cases, the method is comparative, the salt solution being compared with a standard solution, usually potassium dichromate.

A number of experiments are recorded to determine a series of

isosmotic solutions, and the relative concentrations are approximately equal to those of De Vries and Hamburger. The method is also tested by the use of solutions given by De Vries as isosmotic, when the ratios are found approximately equal. The values for the dissociation coefficients as obtained by this method are also compared for a number of salts with those due to Raoult, the agreement, however, being only approximate. The increase of dissociation by dilution can also be found by comparison with an undissociated compound, such as cane sugar. The influence of the plasma is considered, and the author points out that it is merely a diluent unless the salt examined is also present in the plasma. The paper concludes with various details as to the mode of use of the instrument.

L. M. J.

### Mixed Crystals of the Chlorides of Cobalt and Manganese.

By WILLEM STORTENBEKER (*Zeit. physikal. Chem.*, **16**, 250—261).—From solutions of the chlorides of cobalt and manganese containing 1 mol. of cobaltic chloride with from 0 to 5 mols. of manganous chloride mixed crystals can be obtained, red in colour and isomorphous with the hydrated chloride of cobalt,  $\text{CoCl}_2 + 6\text{H}_2\text{O}$ . If the solution contains more than 2 mols. of the manganese salt, violet mixed crystals form spontaneously, isomorphous with the chloride of manganese,  $\text{MnCl}_2 + 4\text{H}_2\text{O}$ . A series of experiments was made with solutions of various strengths, and the percentage of each constituent in both the solution and the crystals determined. At the temperature  $15^\circ$ , it is seen that complete equilibrium exists between the solution  $\text{CoCl}_2 + 2\text{MnCl}_2 + 29\text{H}_2\text{O}$  and the solid phases  $\text{CoCl}_2, 6\text{H}_2\text{O} + 0.59\text{MnCl}_2, 6\text{H}_2\text{O}$ , and  $\text{CoCl}_2, 4\text{H}_2\text{O} + 2.9\text{MnCl}_2, 4\text{H}_2\text{O}$ . The results are also expressed by curves, which are completed to indicate the labile state. The results are also compared with the closely analogous case of the monoclinic and rhombic mixed crystals of the sulphates of iron and magnesium.

L. M. J.

### Method of Determining Molecular Weight and Constitution.

By ISIDOR TRAUBE (*Ber.*, 1895, **28**, 410—418).—According to the author, the molecule of any substance dissolved in water exercises always the same attraction for the solvent, the contraction caused by this attraction being for the gram-molecule 12.2 c.c. In the case of electrolytes, this same contraction is produced by each gram-equivalent of the dissolved ions. The substance is here supposed to retain its original volume on passing into solution, and the contraction is regarded as taking place solely at the expense of the water. The difference, therefore, between the molecular volume of the homogeneous substance  $V_m$  and the molecular solution volume  $v_m$  (this vol., ii, 70) gives the contraction of the water in c.c. per gram-molecule dissolved. It is only in cases in which, in accordance with Ramsay and Shield's method of observation, it is necessary to assume association of the simple gaseous molecules in the liquid state, that the above difference varies to any great extent from 12.2 c.c., and in these cases the number obtained is invariably smaller, the limits being from 1.5 to 12 c.c.

The majority of the organic compounds, according to Ramsay and

Shield's results, are substances in which the association above spoken of does not take place, and which therefore may be regarded as behaving quite normally. With such compounds, the law that has been enunciated may be applied for the purpose of determining molecular weights; for the molecular weight will obviously be that quantity which, taken in grams, produces a contraction, or difference between the molecular volume and the molecular solution volume, of 12.2 c.c. on solution in water.

But the method may be simplified and rendered applicable even to substances insoluble in water. The molecular volume is, in the case of organic compounds, an additive function of the atomic volumes. Up to the present, a satisfactory agreement between the observed values and those calculated on the above assumption has certainly not been obtained, but this the author attributes to two causes. In the first place, no account has hitherto been taken of the association which sometimes takes place in the molecules of liquids, and which has already been spoken of; and, in the second place, it has always been assumed that the molecular volume really is equal to the sum of the volumes of the atoms, and that no change of volume occurs during the formation of the molecule. In the last case, a term would have to be introduced expressing this change of volume,  $A$ , and the formula for calculating the molecular volume from the atomic volumes for organic compounds would be

$$V_m = mV_aC + nV_aH + \dots + A.$$

Now the author has found in the case of the molecular solution volume (*Zeit. anorg. Chem.*, 1895, **8**, 74) that the formation of the molecule from the atoms is always attended by an increase in the total volume. This increase is the same for all substances, both organic and inorganic.  $A$  is therefore positive, and for the molecular solution volume in aqueous solution has a mean value of 13.5, or for the molecular volume of  $13.5 + 12.2 = 25.7$ . From this the following relationships will be found to hold at 15°.

I.  $v_m = m10C + n3.05 H + p10' + q40'' + r60''' + 13.5$ ,  
and

II.  $V_m = m10C + n3.05 H + p10' + q40'' + r60''' + 25.7$ .

$O'$  is hydroxyl oxygen,  $O''$  carbonyl oxygen, and  $O'''$  is ether oxygen, which in this, as in the case of the specific refraction, has a different value. For every benzene ring present, 12.8 units must be subtracted, but the influence of multiple linkages, if any, is so slight that it may be neglected.

With the aid of these formulæ, it is possible by means of a single sp. gr. determination to calculate the molecular weight of any organic compound the constitution of which is approximately known. From the sp. gr., the molecular volume is first calculated, and then, by means of formula I, the molecular solution volume which the substance would have in water. If a correct value has been chosen for the molecular weight, the difference between these two quantities will be approximately 12.2; if the value

chosen is double that which it should be, the difference will be  $2 \times 12.2 + 13.5 = 37.9$ ; and if the value chosen is half the true value, the difference becomes  $\frac{1}{2}(12.2 - 13.5) = -0.7$ . The molecular weight has therefore to be so chosen that the contraction per gram-molecule is 6 to 12.2 c.c.; if double the true molecular weight has been taken, a value from 25.5 to 37.9 may be expected; and with half the molecular weight, a value of  $-0.7$  to  $-3.8$ . The author gives a table of values obtained from the sp. gr. determinations, for hydrocarbons of known molecular weight and of very different constitution, the numbers being all within the limits  $12.2 \pm 4$ .

Since generally the molecular solution volume in a concentrated solution in any organic solvent is equal to the molecular volume of the homogeneous substance, the molecular volume of a solid substance may be ascertained by making a sp. gr. determination of its concentrated solution in some suitable organic solvent. The method is therefore of the widest application, and, from the experimental point of view, is probably the simplest that has been proposed for the determination of molecular weights.

H. C.

**Chemical Equilibria as Temperature Functions.** By JOSEPH E. TREVOR and FREDERICK L. KORTRIGHT (*Amer. Chem. J.*, 1894, 16, 611—624).—The consideration that the only things of which we can take direct cognizance are manifestations of energy, and that the total energy of an isolated system remains constant in amount or, in other words, subsists, leads at once to the idea of the substantiality of energy and to the conception that all natural processes are in their ultimate nature energy transformations. This makes the equilibrium of any material system subject to the condition that a possible variation of any one of the forms of energy which it includes must be exactly compensated by the corresponding variation of the forms correlated with this one; the criterion of equilibrium being that the algebraic sum of the energy changes involved in a virtual displacement of the equilibrium must vanish. When this criterion is applied to the equilibrium between heat  $Q$  and work  $W$ , it furnishes the fundamental differential equation for the equilibria of thermodynamics, in the form

$$\Sigma dW = \frac{Q}{T} dT.$$

$T$  representing the absolute temperature of the heat quantity  $Q$ . This equation contains the theory of all displaceable chemical equilibria, because such equilibria always involve heat, and some one or more entirely convertible forms of energy. There are two cases to be considered, the complete and the incomplete equilibria of the phase rule.

When  $n$  substances compose a chemical system of  $n + 1$  heterogeneous phases, one of which is vapour, the equilibrium is a function of but one independent variable, and its equilibrium equation is

$$+ \frac{p}{T} dT = vdp,$$

or

$$RT d \log_e p - \frac{pT}{T} dT = 0.$$

Here  $p$  is the equilibrium pressure at the temperature  $T$ ,  $\rho$  is the total molecular heat of change, that is, the heat  $Q$  absorbed at constant volume plus  $RT$  the volume energy (normally) obtained, and  $R$  is the constant of the gas-equation  $pv = RT$ . To get rid of the volume energy term, we subtract  $\frac{d \log_e T}{dT} = \frac{1}{T}$  from both members, and there results

$$RT \delta \log_e K - \frac{Q_r}{T} \delta T = 0,$$

$\log_e K$  being the characteristic constant of the reaction isothermal.

When  $n$  independent components make up a system of less than  $n + 1$  heterogeneous phases, the isothermal equilibrium of the system depends, to a greater or less degree, on the relative concentrations of its components, and the balance existing between the respective volume energies of the latter will be disturbed by a possible addition of heat. The sum of the virtual changes then becomes, for a final equilibrium,

$$(\Sigma v dp - \Sigma V dP) - \frac{Q_r}{T} dT = 0.$$

$P$ ,  $V$ ,  $p$  and  $v$  representing the partial pressures and molecular volumes of the originally reacting substances, and of those produced by the reaction respectively. The bracketed member of this equation becomes  $RT \delta \log_e K$  on the elimination of the pressures, and the equation becomes identical with that obtained in the former case, representing therefore the effect of changes of temperature in displacing *all* types of chemical equilibrium under discussion. This equation is usually written in the form

$$\frac{\delta \log_e K}{\delta T} = \frac{Q_r}{RT^2}.$$

In integrating this equation, the heat of reaction is usually assumed to be constant over a very small range of temperature, but this procedure generally restricts its applications. The heat of reaction  $Q_r$  absorbed at the absolute temperature  $T$ , being the energy difference of the reacting systems, is that,  $Q_0$ , at some arbitrarily selected standard temperature  $T_0$  increased for each degree by the excess of the total molecular heat of the system II, which is produced by the reaction over that of the original system I. In symbols

$$Q_r = Q_0 + (c_{II} - c_I)(T - T_0).$$

Making the assumption that the difference  $\Delta c$  of the specific heats is constant between wide temperature limits, we get on substitution of this value for  $Q_r$  and integration

$$\text{Log}_e \frac{K_2}{K_1} = \frac{Q_0 - T_0 \Delta c}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{\Delta c}{R} \log_e \frac{T_2}{T_1}.$$

Successful applications of this relationship are made in the calculation of the heat of vaporisation from the vapour pressure, in the case of water, and of the heat of dissociation of carbonic anhydride as a function

of the temperature. In the latter case, it is shown that at about  $3555^{\circ}$  the value of  $Q$ , the heat of dissociation, passes through zero and changes its sign. H. C.

**Reaction Velocity of Potassium Hypiodite.** By ALFRED SCHWICKER (*Zeit. physikal. Chem.*, 16, 303—314).—By the inter-action of iodine and potassium hydroxide, a mixture of potassium iodide and hypiodite may be considered to be formed, the latter compound passing over into potassic iodate,  $3\text{KIO} = \text{KIO}_3 + 2\text{KI}$ . The author has determined the reaction velocity of this change under various conditions. The method consisted in the determination of the unchanged salt at fixed times from the commencement of the reaction, hydrogen potassium carbonate being added and the precipitated iodine titrated. The reaction being of the third order, the velocity should be given by the equation  $dx/dt = k(A-x)^3$  leading on integration to  $2A^2k = x(2A-x)/t(A-x)^2$  where  $A$  is the original quantity of hypiodite, and  $x$  that after time  $t$ . In those experiments where the iodine was in excess, this expression does give a constant value, and hence the reaction, most probably, takes place as indicated by the above equation. When the potassium hydroxide is in excess, however, the value is not constant, but this condition is fulfilled by  $A/t(A-x)$  indicating that the velocity is given by the equation  $dx/dt = k(A-x)^2$  and that the reaction is hence of the *second* order. What the course of this reaction is, and what is the equation which represents it, are, however, left to future research. L. M. J.

**Rate of Oxidation of Phosphorus, Sulphur and Aldehyde.** By THOMAS EWAN (*Phil. Mag.*, 1894, [5], 38, 505—536, and *Zeit. physikal. Chem.*, 1895, 16, 315—343).—According to our present knowledge, the velocity with which a chemical change takes place is dependent on the concentrations of the substances taking part in the change, and the connection between the two is of such a nature that a greater concentration corresponds with a greater velocity. Under these circumstances, it is of great interest that in a number of instances oxygen gas appears to act, chemically, more vigorously, that is with greater velocity, when it is dilute than when it is more concentrated. The reaction between phosphorus and oxygen is of this character, and was selected by the author in the first place as a suitable one for the study of the connection between the velocity of the change and the concentration of the oxygen.

On the assumption that the rate of the reaction is proportional to the partial pressure of the oxygen, when the volume of the gas is kept constant,  $-dp/dt = K'p$ , where  $p$  is pressure,  $t$  time, and  $K'$  a constant. If  $p = p_0$  when  $t = 0$ ,  $p_0$  being the pressure of the oxygen at the beginning of the experiment, we get on integration

$$K' = \frac{1}{t} \log \frac{p_0}{p}.$$

It was found, however, that the velocity of the reaction in moist air diminishes a little more slowly than the partial pressure of the oxygen, the values of  $K'$  increasing, and therefore that the reaction takes



place somewhat faster at lower pressures than one would expect if its velocity were directly proportional to the pressure. This is probably due to the fact that substances evaporate more rapidly into a gaseous atmosphere when its pressure is small than when it is larger, and as there are reasons for supposing that the phosphorus vapour is oxidised as fast as it is evolved from the surface of the phosphorus, the velocity with which the reaction goes forward will be directly proportional to the rate of evaporation of the phosphorus.

According to Stefan, the rate of evaporation of a liquid into a gas,  $v = c \log P/(P - p')$ , where  $P$  is the total pressure of the gas and vapour,  $p'$  the vapour-pressure of the liquid and  $c$  some constant. Introducing this correction for the changeable velocity of evaporation into the equation already given, we obtain

$$-\frac{dp}{dt} = Kp \log \frac{P}{P - p'}.$$

To integrate this equation we may write  $p = P - a$ , where  $a$  is the partial pressure of the nitrogen and aqueous vapour in the mixture of gases and therefore constant. Then without appreciable error,

$$Kt = \frac{P_0 - P}{p'} + \left( \log \frac{P_0 - a}{P - a} \right) \left[ \frac{a}{p'} - \frac{1}{2} \right].$$

The values of  $K$  are more nearly constant than those of  $K'$  when the partial pressure of the oxygen is from 50 to 150 mm. It appears therefore that the velocity of the reaction in these cases is proportional to the pressure of the moist oxygen. But since, when the pressure of the oxygen is greater than a certain limit, the velocity of the reaction becomes zero, this is not true for all pressures. Determinations of the limiting pressure, above which no reaction takes place, were only made at 20°, when a value of about 700 mm. was obtained. This corresponds with the value given by Joubert for the pressure at which phosphorus just begins to be luminous in oxygen at 20°. Therefore, above a certain limiting pressure (which probably varies with the temperature) the rate of action of moist oxygen on phosphorus is no longer proportional to the pressure of the gas, but is very much slower.

In the action of dried oxygen on phosphorus, quite a different result was obtained. The action began at a much lower pressure than in the former case, and at 21° not until the pressure was reduced to 202 mm. In this case, the velocity of the reaction is not proportional to the pressure itself, but seemingly to the square root of the partial pressure of the oxygen. This is only true, however, at 20°, up to a pressure of 60—70 mm.; above this pressure, the velocity decreases.

Somewhat similar results to those obtained with dry oxygen and phosphorus were obtained with sulphur and oxygen. The experiments were conducted at the temperature of boiling turpentine. The velocity of the action is proportional to the square root of the pressure rather than to the pressure itself.

Experiments with aldehyde vapour and oxygen led to the conclusion

that these react with formation of acetic acid with a velocity which is proportional to the pressure of the aldehyde vapour and to the square root of the pressure of the oxygen. It is possible that a pressure of oxygen exists above which this is no longer true.

The results with aldehyde vapour show the probability of the existence of free atoms in oxygen. There can be little doubt, from analogy, that the oxygen molecule would, at a sufficiently high temperature, be dissociated into its atoms. Equilibrium will be established when the concentration of the atoms has reached a certain value determined by the equation  $C_{(O_2)} = k C_{(O)}^2$ , where  $C_{(O_2)}$  is the concentration of the oxygen molecules, and  $C_{(O)}$  that of the atoms.  $k$  is a constant which depends on the temperature. The equilibrium will change with falling temperature in such a way that the concentration of the oxygen atoms will diminish. It will, however, probably never become nothing. If this is true at ordinary temperatures, we shall have

$$C_{(O)} = \text{const.} \sqrt{C_{(O_2)}}.$$

As the concentration of the oxygen atoms is small, we can put the concentration of the oxygen molecules proportional to the pressure of the gas, and the concentration of the oxygen atoms will then be proportional to the square root of the pressure of oxygen. If we assume therefore that the atoms alone take part in the oxidation of the aldehyde, we shall have the velocity of the action always proportional to the square root of the pressure of the oxygen.

Possibly in the case of sulphur and phosphorus with dry oxygen, the reaction takes place in stages. The velocity of the whole reaction would then be the sum of the velocities of the partial reactions, each one of which would be proportional to the concentration of the oxygen atoms.

H. C.

**Apparatus for Fractional Distillation under Very Low Pressures.** By GEORG W. A. KAHLBAUM (*Ber.*, 1895, 28, 392—395).—This apparatus is designed for distillations under a pressure of, say, 3 mm., the mercury pump being used; it is illustrated by means of a sketch. All the joints are made air-tight with mercury seals, and the receiver has a slightly novel construction, the drops falling into little cups attached to a central vertical tube (which can be turned on its axis) down which they flow and by which they are directed into flasks attached underneath.

C. F. B.

**Laboratory Apparatus.** By C. V. SCHON (*J. pr. Chem.*, 1895, [2], 51, 100—102).—The author describes a form of apparatus for the distillation of zinc methyl in an atmosphere of carbonic anhydride; and another arrangement by means of which a gas can be conveniently passed through a liquid containing a solid in suspension, the delivery tube being at the same time rotated so as to stir the liquid.

A. H.

**Improved Laboratory Apparatus.** By JAKOB VOLHARD (*Annalen*, 1895, 284, 233—244).—The disadvantages of the constant-level water bath in general use are pointed out; it is shown that these may be overcome by introducing a few structural modifications, and employing one reservoir of distilled water to supply all the water baths of a laboratory.

An apparatus for heating sealed tubes to high temperatures is described, in which the vapour of boiling petroleum is used as a substitute for air. A copper boiler, pierced longitudinally by two cylindrical tubes, opens, on its upper surface, into a metallic condenser of such construction, that until it approaches the boiler, the condensed petroleum is separated from the ascending vapour. By means of a three-way tap in the tube through which the condensed petroleum travels, the apparatus may be used either as a distillation or reflux apparatus. Commercial petroleum, which begins to boil at about 130°, is introduced into the boiler, and the more volatile portions distilled off until the boiling point of the liquid reaches the temperature at which it is required to heat the tubes. The latter are enclosed in wrought-iron cylinders, welded at one end to an iron plate, and closed at the other with a screw-cap; an iron shield at this end of the furnace renders the apparatus free from danger.

By a simple modification in the form of the tiles, the author has increased the efficiency of the ordinary combustion furnace; the consumption of gas under the new conditions is very considerably lessened.

M. O. F.

**A New Shaking and Stirring Apparatus.** By EWALD SAUER (*Ber.*, 1895, 28, 559—560).—This is driven by a hot-air engine, and will shake a 6-litre bottle, or a framework containing 4 to 8 bottles of 500 c.c. capacity, and, at the same time, will drive 6 to 10 Witt's stirrers, a centrifugal machine, a mill, &c.

C. F. B.

**An Extremely Simple Centrifugal Apparatus.** By GEORG W. A. KAHLBAUM (*Ber.*, 1895, 28, 391—392).—The apparatus consists of two test-tubes, the one sliding in the other; the inner tube has its end cut off, and closed by a piece of platinum gauze melted on to the glass. The crystalline magma is placed in the inner tube, which is then closed with a cork, and the whole apparatus is whirled round at the end of a string attached to the open end of the outer test-tube.

C. F. B.

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### Inorganic Chemistry.

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**Solubility of Ozone in Water.** By L'ABBÉ MAILFERT (*Compt. rend.*, 1894, **119**, 951—953).—The solubility of ozone in water can be demonstrated by the odour of the solution, its action on silver oxide and on mercury, and the formation of hydrogen peroxide in contact with ether. The solubility was determined by allowing highly

ozonised oxygen to remain in contact with water for some days, and then estimating the quantity of ozone both in the solution and in the residual gas. The results are given in the following table, the coefficient of solubility being the ratio of the weight of ozone in 1 litre of water to the weight of ozone in 1 litre of the residual gas.

T°.	0°.	6°.	11.8°.	13°.	15°.	19°.	27°.
Milligrams of ozone in } 1000 c.c. of water.. }	39.4	34.3	29.9	28.0	25.9	21.0	13.9
Coefficient of solubility	0.641	0.562	0.500	0.482	0.456	0.381	0.270

T°.	32°.	40°.	47°.	55°.	60°.
Milligrams of ozone in } 1000 c.c. of water.. }	7.7	4.2	2.4	0.6	0.0
Coefficient of solubility	0.195	0.112	0.077	0.031	0.000

Ozone is much more soluble than oxygen. The solubility is the same in acidified water as in pure water up to 20°, but is greater at higher temperatures.

T°.	30°.	33°.	42.7°.	49°.	57°.
Coefficient of solubility in } acidified water..... }	0.240	0.224	0.174	0.156	0.096

It seems possible that aqueous solutions of ozone may be valuable as sterilisers or disinfectants.

C. H. B.

**Phosphorus Chloronitride and two of its Homologues.** By HENRY N. STOKES (*Ber.*, 1895, 28, 437—439).—When phosphorus chloronitride,  $P_3N_3Cl_6$ , is prepared by distilling a mixture of ammonium chloride and phosphorus pentachloride, two compounds of the same empirical formula are also obtained in small quantity.

*Phosphorus chloronitride*,  $P_3N_3Cl_6$ , crystallises from benzene in prisms. It melts at 123.5° (corr.), and boils at 328.5°; it is not very volatile in an atmosphere of steam. Boiling water, acids, and alkalis are without action on it, but when the ethereal solution is agitated with water for four hours, a crystalline chlorhydrin is produced, undergoing conversion into *tetrametaphosphinimic acid*,  $P_4N_4O_8H_8 + 2H_2O$ , a remarkably stable acid, which yields three series of salts. The analogous *trimetaphosphinimic acid*,  $P_3N_3O_6H_6$ , is obtained from the previously known chloronitride, and the intermediate product is a crystalline *chlorhydrin*,  $P_3N_3Cl_4O_2H_2$ . The *chloramide*,  $P_3N_3Cl_4(NH_2)_2$ , is obtained by agitating the ethereal solution of the chloronitride with aqueous ammonia; it crystallises from water.

An oily compound,  $(PNCl_2)_x$ , is also obtained by distilling a mixture of ammonium chloride and phosphorus pentachloride. It is not volatile in an atmosphere of steam, and is indifferent towards boiling water. Agitation of the ethereal solution with water, however, gives rise to a crystalline metaphosphinimic acid, which is decomposed into tetrametaphosphinimic acid and ammonium phosphate by the action of boiling water.

M. O. F.

**The Arsenites.** By ALFRED STAVENHAGEN (*J. pr. Chem.*, 1895, [2], 51, 1—42).—The author has reinvestigated the arsenites of a large

number of the metals, and has succeeded in preparing a number of new salts. In some cases it was found impossible to obtain salts which had been previously described, whilst in other cases the salts, prepared according to the description of previous authors, were found to have a different composition from that which had been assigned to them.

New salts.	Salts previously described.	Author's results with salts previously described.
$K_3AsO_3$	$KAsO_2$ (Pasteur) . . . . . $K_4As_2O_5$ (Pasteur) . . . . . $K_2As_4O_7 + 2H_2O$ (Pasteur) $K_4As_6O_{11} + 3H_2O$ (Bloxam) ..	Not obtained pure. $K_4As_2O_5 + 6H_2O$ .
$Na_3AsO_3$	$NaAsO_2$ (Pasteur) . . . . . $Na_3As_2O_5$ (Pasteur) . . . . . $(NH_4)AsO_2$ (Pasteur and Luyne)	Could not be obtained. Composition could not be determined with certainty.
$(NH_4)_3AsO_3$ (?)	$(NH_4)_2As_2O_5$ (Stein) . . . . . $Ca_3(AsO_3)_2$ (Kühn) $Ca(AsO_2)_2$ (Simon) $Ca_2As_2O_5 + H_2O$ (Stein, Simon, Bloxam) $Ca_3As_4O_9 + 3H_2O$ (Stein) . . . . $Sr(AsO_2)_2 + 4H_2O$ (Stein) . . . .	Composition could not be determined with certainty.
$Sr_3(AsO_3)_2$ (?)	$Bu(AsO_2)_2$ (Filhol)	Could not be obtained.
$Sr_2As_2O_5 + 2H_2O$	$Ba_2As_2O_5 + 4H_2O$ (Stein)	Not obtained pure.
$Ba_3(AsO_3)_2$	$BaH_4(AsO_3)_2$ (Bloxam) . . . . . $Mg_3(AsO_3)_2$ (Stein) . . . . .	$Ba_2As_2O_5 + 2H_2O$ . Could not be obtained. Could only be obtained by a new method.
	$MgAs_2O_5$ (Bloxam) $Mg_2As_2O_5 + H_2O$ (Bloxam) .. $Zn_3(AsO_3)_2$ (Eloxam)	Could not be obtained.
$Cd_3(AsO_3)_2$	—	
$Hg_3AsO_3$	—	
$Hg_3(AsO_3)_2$ (?)	—	
$Cu_3AsO_3$ (?)	$CuHAsO_3$ (Bloxam) . . . . .	Could not be obtained pure.
$Cu(AsO_2)_2 + 2H_2O$	— $Ag_3AsO_3$ (Pasteur) $Ag_4As_2O_5$ (Pasteur) . . . . . $Ag_6As_4O_9$ (Girard) . . . . .	Could not be obtained pure. Could not be obtained.
$AuAsO_3 + 2H_2O$	—	
$Tl_3AsO_3$	—	
$Sn_3(AsO_3)_2 + H_2O$	—	
$Sn_3(AsO_3)_4 + 5\frac{1}{2}H_2O$	— $Pb_3(AsO_3)_2 + H_2O$ (Kühn- Streng) $Pb(AsO_2)_2$ (Berzelius) $Pb_2As_2O_5$ (Berzelius, Filhol)	
$BiAsO_3 + 5H_2O$ (?)	— $CrAsO_3$ (Neville) . . . . . $Mn_3H_2As_2O_{10} + 4H_2O$ (Stein) $Co_2As_2O_5$ (Girard) $Co_3As_4O_9 + 4H_2O$ (Girard) .. $Ni_2As_2O_5$ (Girard) . . . . . $Ni_3As_4O_9 + 4H_2O$ (Girard)	Could not be obtained. Not obtained pure.
$Mn_3(AsO_3)_2 + 3H_2O$	—	
$Co_3(AsO_3)_2 + 4H_2O$	—	
	—	
$Pt_3(AsO_3)_4$	—	

The arsenites may be considered as derived from ortho-arsenious acid,  $\text{H}_3\text{AsO}_3$ ; meta-arsenious acid,  $\text{HAsO}_2$ ; or pyro-arsenious acid,  $\text{H}_4\text{As}_2\text{O}_5$ .

The table on p. 218 summarises the results obtained. The methods of preparation and properties are given in detail in the original.

The substances marked (?) were not obtained perfectly pure. The most important memoirs to which reference is made are the following: Simon, *Ann. Phys. Chem.*, 1837, **40**, 442; Pasteur, *Annalen*, 1848, **68**, 309; Stein, *Annalen*, 1850, **74**, 218; Girard, *Compt. rend.*, 1852, **34**, 918; *Annalen*, 1852, **84**, 254; 1853, **88**, 249; Kühn, *Arch. Pharm.*, [2], **69**, 267.

The author was unable to prepare a definite compound of arsenious oxide with ferric hydroxide. It is possible that the action of ferric hydroxide as an antidote in cases of poisoning by arsenious oxide is due to the fact that it prevents the reduction of the oxide to arsine, to the formation of which the author is inclined to ascribe the fatal effects.

A. H.

**Graphite.** By HENRI MOISSAN (*Compt. rend.*, 1894, **119**, 976—980).—The author has investigated the rate of oxidation, the ignition points, and the sp. gr. of the different varieties of graphite obtained by (1) heating diamond in an arc produced by a current of 350 ampères and 70 volts, (2) condensation of sublimed carbon on the positive electrode, (3) the alteration of the extremities of the electrodes, (4) condensation of sublimed carbon on a cooled tube, (5) the action of an arc (as above) on carbon from sugar, (6) the action of a current of 2200 ampères and 60 volts on wood-charcoal contained in a crucible in the electric furnace. Similar determinations were made with the graphite obtained by saturating aluminium, manganese, nickel, chromium, tungsten molybdenum, uranium, zirconium, and vanadium with carbon in the electrical furnace, the metal being removed by treatment with chlorine, and the amorphous carbon by the action of fuming nitric acid on the residue.

The graphite thus obtained may be amorphous or crystalline. Its sp. gr. varies between 2.10 and 2.25, and its temperature of ignition in oxygen is about  $660^\circ$ . There are several varieties of graphite, just as there are several varieties of amorphous carbon, and their stability, and in particular their resistance to the action of a mixture of potassium chlorate and nitric acid, increases with the temperature to which the graphite was subjected.

When graphite is treated with fuming nitric acid and potassium chlorate in the manner described by Berthelot, the oxidation is somewhat slow, and the colour of the graphitic oxide varies from green or deep maroon to yellow. If, however, the nitric acid is prepared by the action of a large excess of boiled sulphuric acid on recently fused potassium nitrate, and the potassium chlorate is carefully dried, oxidation of the graphite is more rapid, and the graphitic oxide is yellow or almost colourless. The quantity of potassium chlorate necessary is from 20 to 30 times the weight of the graphite, and the oxidation must be completed at  $60^\circ$ , although care must be taken that

the temperature does not rise to this point in the early stages of the reaction.

C. H. B.

**Displacement of Carbon from Fused Cast Iron by Boron and Silicon.** By HENRI MOISSAN (*Compt. rend.*, 1894, 119, 1172—1175).—When grey cast iron containing about 3·2 per cent. of carbon is strongly heated in a porcelain boat brasqued with boron and contained in a porcelain tube through which a current of hydrogen is passed, the boron displaces the carbon, which is reduced to 0·36—0·14 per cent., whilst at the same time the quantity of slag present in the iron is considerably reduced because the boron combines readily with the impurities. The residual iron contains 8 to 9 per cent. of boron. Similar effects are observed with white cast iron, the carbon in one case being reduced from 3·85 to 0·24 per cent., and the slag from 0·36 to 0·06 per cent. When cast iron containing 10 per cent. of boron is added to 10 times its weight of grey cast iron fused in a forge, there is still a notable displacement of carbon, and the metal has a lamellar structure, is very hard, and resembles white cast iron in appearance.

Crystallised silicon, under similar conditions, displaces carbon from grey or white cast iron, the carbon separating in the form of graphite. The same effect is observed with fused silicon and a highly carburised iron prepared in the electric furnace from soft iron and sugar-charcoal, the carbon separating as brilliant crystals of graphite.

The fact that the displacement of carbon by silicon is not quite complete is probably due to the establishment of a state of equilibrium between the iron silicide and the iron carbide, the conditions of equilibrium varying with the temperature and with the impurities which are always present in white or grey cast iron.

C. H. B.

**Graphites from Iron.** By HENRI MOISSAN (*Compt. rend.*, 1894, 119, 1245—1250).—The author has investigated the graphites formed in cast iron under various conditions of temperature and pressure.

Graphite from grey cast iron which melts at about 1150° can be separated from the metal and the amorphous carbon by successive treatments with chlorine at a dull red heat, fuming nitric acid, and hydrofluoric acid; its sp. gr. is 2·17, and it ignites in oxygen at 670°. If the metal is treated with hydrochloric acid mixed with a little nitric acid, instead of being heated in chlorine, and the residue is washed and dried, and then subjected to several treatments with fuming nitric acid, followed by hydrofluoric acid, and, finally, concentrated sulphuric acid, the graphite obtained contains only 80 to 85 per cent. of carbon, 1·30 per cent. of ash, and 0·15 to 0·80 per cent. of hydrogen. It would seem therefore that in the action of the acids on the metal a complex compound of carbon, hydrogen, oxygen, and perhaps also nitrogen, is formed, and is not decomposed even when the graphite is heated at 400°. The possible formation of such compounds, which is probably the result of the hydrogenisation, followed by oxidation, of the iron carbide, should be taken into account in all investigations of the graphites obtained from metals (compare preceding abstract).



When soft iron, mixed with an excess of carbon from sugar, is heated in a carbon crucible in the electric furnace with a current of 2000 ampères and 60 volts for 10 minutes, the iron dissolves large quantities of carbon, and becomes so pasty that the crucible can be inverted without the contents running out. The graphite obtained from this iron ignites in oxygen at about  $650^{\circ}$ ; it contains only 0.28 per cent. of hydrogen, and is therefore much purer than graphite from ordinary cast iron; sp. gr. = 2.18. It is oxidised with considerable difficulty.

In order to ascertain the effect of pressure, the fused iron containing carbon was suddenly cooled by immersion in water (Abstr., 1893, ii, 275). The graphite then obtained is in the form of short crystals with blunted angles, and of irregular masses which have the appearance of incipient fusion; sp. gr. = 2.16; temperature of ignition in oxygen  $660^{\circ}$ . It contains 0.64 per cent. of hydrogen and 1.29 per cent. of ash.

The graphite displaced from cast iron by silicon (preceding abstract) forms very regular black crystals of sp. gr. 2.20; it contains 0.2 per cent. of hydrogen, 0.85 per cent. of ash, and 98.82 per cent. of carbon. This form of graphite is readily oxidised.

Graphite separated from cast iron saturated with carbon in the electric furnace was allowed to cool out of contact with air, and was then heated in a vacuum at  $500^{\circ}$ , and afterwards burnt in oxygen. No water was formed, and it follows that hydrogen does not pre-exist in graphite, but is a result of the hydrogenisation of the iron carbide, or perhaps of the amorphous carbon, under the influence of reagents.

The general conclusion is that at the ordinary pressure the graphite is purer; it is also less easily attacked by a mixture of nitric acid and potassium chlorate the higher the temperature at which it is obtained. The small quantity of hydrogen present in graphite diminishes as the purity increases.

C. H. B.

**Intumescent Graphite.** By HENRI MOISSAN (*Compt. rend.*, 1895, 120, 17—19).—The author has previously described (Abstr., 1893, ii, 320) a method of preparing intumescent graphite by dissolving carbon in melted platinum. His later experiments prove that graphite obtained simply by the action of a high temperature on any form of carbon, or by the condensation of carbon vapour, shows no trace of intumescence when treated with strong nitric acid; on the other hand, all the graphites obtained by dissolving carbon in some metal at a high temperature are intumescent. It would seem that the temperature is at least as important as the action of the metal; the graphite from grey cast iron showed no intumescence, but after the metal had been heated in the electric furnace with a current of 2000 ampères and 50 volts the graphite was highly intumescent.

For all varieties of intumescent graphite produced at a high temperature, the temperature of intumescence lies between  $165$  and  $175^{\circ}$ . If a small quantity of the graphite is treated with nitric acid, dried at a gentle heat, and then more strongly heated in a vacuous tube, it gives off a mixture of carbonic anhydride, nitrogen, and nitrogen

oxides, whilst a small quantity of nitric acid condenses on the sides of the tube. This result confirms the author's view (*loc. cit.*) that the intumescence is due to the sudden liberation of heated gases.

Natural intumescent graphites seem to have been produced at a somewhat high temperature, but not under very great pressure, in the midst of masses of iron which have since disappeared.

C. H. B.

**Carbon Monosulphide.** By ALBERT DENINGER (*J. pr. Chem.*, 1895, [2], 51, 346—349).—Carbon monosulphide appears to be formed when sodium sulphide is heated with chloroform at  $180^{\circ}$ , and when silver iodide is heated with iodoform. It is best obtained, mixed with hydrogen, by bringing 15 grams of sodium into 125 c.c. of dry aniline, and adding 150 c.c. of carbon bisulphide. A gas is given off which is passed through aqueous soda, over india-rubber, and, finally, through triethylphosphine. It readily burns with a blue flame forming sulphurous anhydride. The gas is very readily absorbed by alcohol and aniline, has a pleasant smell of (pure) carbon bisulphide, and condenses in a freezing mixture to a very volatile liquid, the constants of which have not been determined. When mixed with oxygen and ignited, it explodes violently.

A. H.

**Preparation of Amorphous Silicon.** By VIGOUROUX (*Compt. rend.*, 1895, 120, 94—96).—Amorphous silicon is readily obtained by the action of magnesium on silica, provided that the materials are quite dry, and that the action is moderated by the presence of magnesium oxide. In absence of the oxide, the temperature of the reaction is too high, and some of the silicon is fused. Silica is not so satisfactory as magnesia for this purpose.

Powdered quartz and magnesium powder such as is used for photographic purposes are mixed in the calculated proportions, and to the mixture is added one-fourth of its weight of calcined magnesia. The three substances are very intimately mixed and placed in a fire-clay crucible, which they must not more than half fill. A layer of magnesia is placed on the top, and the crucible is then heated at  $300\text{--}400^{\circ}$ , in order to thoroughly dry the contents. The crucible with its cover is then heated to redness for a few minutes, and as soon as the action ceases it is allowed to cool. Reduction takes place at  $540^{\circ}$ . If the mixture is placed on a plate and covered with magnesium powder, and the latter is ignited, reduction spreads throughout the mass.

The product is heated with hydrochloric acid, then with boiling sulphuric acid, then two or three times alternately with hydrofluoric acid and sulphuric acid, and, finally, with hydrochloric acid. After drying, the silicon forms a maroon coloured, homogeneous powder containing only 1.0 to 0.4 per cent. of impurities. Any small globules of fused silicon can, if necessary, be removed by levigation.

C. H. B.

**Constitution of Silver-Ammonia Compounds.** By ALBERT REYCHLER (*Ber.*, 1895, 28, 555—558).—The electrical conductivity of, and depression of freezing point caused by, the compounds of ammonia with silver nitrate, nitrite, acetate, and sulphate, and with

copper nitrate and nitrate have been examined. It is found that ammonia in the proportion of  $2\text{NH}_3$  per equivalent of silver or copper is taken up without the molecular depression or equivalent conductivity being altered; ammonia present in excess of this quantity does affect these values, and hence is split off in solution. The firm fixation of a second  $\text{NH}_3$ -group is not in accord with the old theory of silver-ammonia compounds. The author prefers to explain the facts in terms of his own theory of the nature of solutions (Abstr., 1893, ii, 315).

C. F. B.

**Silver Sulphide.** By ALFRED DITTE (*Compt. rend.*, 1895, 120, 91—93).—When silver sulphide is allowed to remain in contact with a cold saturated solution of potassium monosulphide out of contact with light, it is gradually converted into red crystals of the double sulphide  $4\text{Ag}_2\text{S} \cdot \text{K}_2\text{S} + 2\text{H}_2\text{O}$ , which forms brilliant plates composed of microscopic needles. In very thin films, it transmits garnet-red light. The same compound can be formed in hot solutions, but the solution of alkali sulphide must be highly concentrated and the product is liable to be impure.

The silver potassium sulphide changes when exposed to light, and becomes dark grey; it is decomposed by water, especially on heating, with separation of black silver sulphide. In presence of cold water a condition of equilibrium is established between the water, the double sulphide and the simple sulphides resulting from its decomposition. A solution of 300 grams of potassium monosulphide per litre has no action on the double sulphide at  $5^\circ$ . It is clear that if an aqueous solution can be prepared which acts neither on silver sulphide nor on the double sulphide, except to dissolve small quantities of the latter, and if this liquid undergoes small changes of temperature sufficient to decompose the dissolved double sulphide, the conditions will be favourable to the formation of crystallised silver sulphide. As a matter of fact, a solution of 350 grams of potassium monosulphide per litre at  $20^\circ$  converts amorphous silver sulphide after some days into grey-black lustrous crystals.

A cold saturated solution of sodium sulphide does not contain sufficient of the salt to admit of the formation of a double sulphide, but a hot solution containing 800 grams of the anhydrous sulphide per litre converts silver sulphide into red crystals of the double sulphide,  $3\text{Ag}_2\text{S} \cdot \text{Na}_2\text{S} + 2\text{H}_2\text{O}$ . It is decomposed by cold water and also by a cold saturated solution of sodium sulphide.

A hot highly concentrated solution of sodium sulphide converts silver sulphide into a vermilion coloured, crystalline powder which, however, it is difficult to obtain pure.

C. H. B.

**Solubility of Strontium Bromide in Alcohol.** By FONZES-DIACON (*J. Pharm.*, 1895, [6], 1, 59).—The solubility of anhydrous strontium bromide in alcohol is practically constant between  $0^\circ$  and  $40^\circ$ , 100 c.c. of absolute alcohol dissolving about 64.5 grams of the anhydrous salt and forming a solution having a sp. gr. = 1.210 at  $0^\circ$ . When left in closed flasks, this solution deposits large, orthorhombic prisms of the composition  $2\text{SrBr}_2 \cdot 5\text{EtOH}$ .

L. T. T.

**Valency of Beryllium.** By ALPHONSE COMBES (*Compt. rend.*, 1894, 119, 1221—1223).—Beryllium is now generally regarded as bivalent, the formula of its oxide being  $\text{BeO}$ , but Hautefeuille's observation that beryllia can partially replace alumina in certain silicates and Wyruboff's observation that beryllium silicotungstates are isomorphous with aluminium silicotungstates but not with the magnesium compounds, make further proof of the bivalent character of beryllium desirable.

*Beryllium acetylacetonate* is readily obtained as a white crystalline precipitate by mixing solutions of equivalent quantities of beryllium acetate and acetylacetone; it is very slightly soluble in cold water but more soluble in hot water, and very soluble in alcohol from which it crystallises in large crystals belonging to the rhombic system, whereas the aluminium compound crystallises in the monoclinic system. Beryllium acetylacetonate melts at  $108^\circ$ , sublimes partially at  $100^\circ$ , and boils at  $270^\circ$  under ordinary pressure without decomposing. Two determinations of the vapour density, the first at the boiling point of diphenylamine, and the second at the boiling point of mercury, gave the values 7.26 and 7.12 respectively. The value calculated for  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ , where  $\text{Be} = 9$ , is 7.16, whilst the value for  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$ , where  $\text{Be} = 13.5$ , is 10.75.

It follows that beryllium is bivalent, and the formula of its oxide is  $\text{BeO}$ . (Compare Abstr., 1889, 571.) C. H. B.

**Zinc and Manganese Sulphides and the Protomorphic State.** By A. VILLIERS (*Compt. rend.*, 1895, 120, 97—99).—The author applies the term *protomorphic state* to the condition in which nickel, cobalt and zinc sulphides and other compounds exist at the moment of their formation.

In the case of zinc sulphide the change is very rapid in hot solutions, but comparatively slow at the ordinary temperature. Thomsen found (Abstr., 1879, 206) that a solution of sodium sulphide gives an immediate precipitate with zinc sulphate; with sodium hydrosulphide, on the other hand, the precipitate is formed if the two substances are mixed in equivalent proportion, but only an opalescent liquid is obtained if double the proportion of hydrosulphide is added.

The author finds that if zinc sulphate is added to sodium hydroxide solution until the precipitate just ceases to redissolve, and hydrogen sulphide is passed into the liquid, there is at first a precipitate, but this completely redissolves if the passage of the gas is continued, provided that the solution contains not more than 1 per cent. of zinc sulphate. If the liquid is boiled or is mixed with alkalis or dilute acids, zinc sulphide is precipitated.

If, in the experiment just described, the passage of hydrogen sulphide ceases when a precipitate is formed, and the vessel is then closed, allowed to remain for some hours at the ordinary temperature, and again treated with a current of the gas, the precipitate will not redissolve, and hence has undergone some change. The soluble modification of zinc sulphide is always amorphous, the insoluble is always crystalline. The behaviour of zinc sulphide when precipitated

from alkaline solutions by hydrogen sulphide, may cause errors in analysis, and it is always better to precipitate in presence of acetic acid.

No evidence of a change of state could be obtained in the case of manganese sulphide. C. H. B.

**Constitution of Inorganic Compounds.** By ALFRED WERNER (*Zeit. anorg. Chem.*, 1895, **8**, 153—188 and 189—197).—Two theoretical papers dealing with the constitution of the ammonio-metallic compounds. (Compare Jörgensen, *ibid.*, **5**, 147, and **7**, 289; and Werner, *ibid.*, **3**, 267.) E. C. R.

**Double Decomposition between Gaseous Compounds.** By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1895, **8**, 213—223).—When two compounds, capable of acting on one another so that one of the products is removed from the sphere of action as it is formed, are mixed in the form of vapour, a double decomposition takes place in a similar way to the double decomposition so well-known in aqueous solution.

The author has examined the action of hydrogen sulphide on several volatile salts; the method of procedure being as follows:—the salt is placed in a hard glass tube, and dry hydrogen passed over it. In the front part of the tube some sulphur is placed, and when the air is completely expelled, the sulphur is heated so that hydrogen sulphide is produced; at the same time the salt is volatilised. The tube is heated at 400—450°. With mercuric chloride, a reaction at once takes place and the black modification of mercury sulphide described by Spring (this vol., ii, 110) is formed. The product is crystalline, and shows the characteristic habit of natural metacinnabarite. When sulphur vapour is mixed with mercuric chloride vapour by means of a current of carbonic anhydride, no action takes place, showing that the mercury sulphide is the product of the double decomposition of hydrogen sulphide and mercuric chloride. Ferric chloride when treated in the same way yields a greyish-black, crystalline powder which under the microscope is seen to contain lustrous, yellow crystals.

The following sulphides have been prepared in the same manner. Antimony sulphide,  $\text{Sb}_2\text{S}_3$ , in crystals identical with the natural compound; when the action takes place at a higher temperature, beautiful long lustrous plates are formed. Arsenic trichloride is decomposed in a similar manner, and arsenic burns with a dark blue flame. Tin sulphide is obtained from the chloride in small, golden aggregates. Molybdenum pentachloride yields an extremely fine powdery sulphide and the tube becomes covered with a mirror.

E. C. R.

**The Molecular Weight of Mercurous Chloride.** By MICHELE FILETI (*J. pr. Chem.*, 1895, [2], **51**, 197—204).—The author criticises the experiments of Harris and V. Meyer (*Abstr.*, 1894, ii, 353) and the conclusions drawn from them. He maintains, in answer to V. Meyer's latest remarks on the subject (this vol., ii, 46), that a complete dissociation of mercurous chloride does not occur, in which case the formula for this compound cannot be  $\text{Hg}_2\text{Cl}_2$ , for its vapour density

is 8.14, and not between this number and 16.28. No experiment which Meyer has quoted shows that mercuric chloride vapour does not prevent, or at any rate hinder, the dissociation of mercurous chloride; all analogy is in favour of such prevention, and the author claims that his original determinations show that the molecular formula in question is  $\text{HgCl}$ . (Compare further V. Meyer, this vol., ii, 166.) A. G. B.

**Reduction of Aluminium by Carbon.** By HENRI MOISSAN (*Compt. rend.*, 1894, 119, 935—937).—Many reactions that are limited at ordinary high temperatures become complete in the electric furnace in consequence of the much higher temperature obtainable. Barium carbonate, for instance, is completely decomposed. Aluminium oxide has hitherto been regarded as irreducible by carbon, but if corundum is placed in a carbon dish and heated in the carbon tube of the electric furnace with a current of 1200 ampères and 80 volts, it is completely volatilised in a few minutes, and the condensed crystals of alumina and graphite are mixed with small spheres of aluminium. If alumina is heated in a carbon tube, closed at one end, with a current of 300 ampères and 65 volts, the volatilised alumina contains some reduced aluminium. Fused alumina remains in the lower part of the tube, and against the walls of the latter, where the temperature was highest, there are small white or yellowish globules of a mixture of aluminium and aluminium carbide. More marked results of the same kind are obtained by heating a mixture of alumina and starch under the same conditions. The cooled residue in the tube is always covered with a layer of graphite formed by the condensation of volatilised carbon.

At a somewhat lower temperature, alumina can remain fused in contact with carbon without any reduction taking place. Reduction is in fact due to the interaction of alumina vapour and carbon vapour at a high temperature. If the temperature is not sufficiently high, the two vapours may mix without reacting. C. H. B.

**Hydrated Metallic Chlorides.** By PAUL SABATIER (*Bull. Soc. Chim.*, 1894, [3], 11, 546—549; compare *Abstr.*, 1889, 1049, and Lescœur, *Abstr.*, 1893, ii, 364, and 1894, ii, 343).—A question of priority with Lescœur, and a criticism of some of his work.

Tetrahydrated manganous chloride effloresces in a dry atmosphere under low pressure to a hydrate containing  $\frac{5}{3}\text{H}_2\text{O}$ , and not  $2\text{H}_2\text{O}$ ; the same salt is obtained by saturating the solution of the tetrahydrate with hydrogen chloride. The two hydrates resemble those of ferric chloride,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  and  $5\text{H}_2\text{O}$ , in containing respectively  $2\text{H}_2\text{O}$  and  $\frac{5}{3}\text{H}_2\text{O}$  per atom of chlorine.

Hexahydrated magnesium chloride yields the pentahydrate under the above conditions as previously observed by Miller and predicted by Thomsen from thermochemical considerations.

Ferrous chloride is normally tetrahydrated, as observed by Berzelius and others, and not hexahydrated; under the above treatment, it is converted into the white or pale green dihydrate observed by Jonas,

but if the solution is not completely saturated with the hydrogen chloride, the tetrahydrate is sometimes precipitated unchanged.

Copper chloride crystallises from aqueous solutions as a dihydrate; Lescœur's dark yellow monohydrate cannot be stable, as the dihydrate readily loses all its water in a dry atmosphere under low pressure.

JN. W.

**Iron Chromates.** By CHARLES LEPIERRE (*Compt. rend.*, 1894, 119, 1215—1218).—No ferrous chromates seem to exist. When saturated solutions of ferrous sulphate with chromic acid or alkali chromates or dichromates are mixed at low temperatures, the chromate is reduced and basic ferric sulphates are formed. If the ferrous salt is in excess, the product is a ferrosiferrous sulphate.

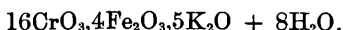
The action of ferrous sulphate (6 mols.) on potassium chromate (2 mols.) at 0° yields the compound  $2\text{CrO}_3, 6\text{Fe}_2\text{O}_3, 3\text{K}_2\text{O}$ , which is washed with water, alcohol, and ether at 0°; when moist, it is brown, and when dried, black. After drying in the air, it retains about 30 per cent. of water. The action of ferrous sulphate on potassium chromate at higher temperatures yields only basic ferric sulphates.

The action of excess of potassium chromate on ferrous sulphate yields a yellowish-brown, micro-crystalline precipitate of the composition  $4\text{CrO}_3, 3\text{Fe}_2\text{O}_3, 4\text{K}_2\text{O}$ , which retains 22·7 per cent. of water when dried in the air. Similar results are obtained with ammonium ferrous sulphate, the precipitate being  $10\text{CrO}_3, 6\text{Fe}_2\text{O}_3, 7\text{K}_2\text{O}$ . With sodium chromate, the precipitate is  $5\text{CrO}_3, 7\text{Fe}_2\text{O}_3, 4\text{Na}_2\text{O}$ , and with ammonium chromate,  $6\text{CrO}_3, 5\text{Fe}_2\text{O}_3, 6(\text{NH}_4)_2\text{O}$ . With ammonium and sodium dichromates, there is immediate oxidation without formation of chromates.

The addition of a saturated solution of potassium chromate to an excess of a saturated solution of ferric chloride yields ruby-red, hexagonal crystals of the composition  $11\text{CrO}_3, 3\text{Fe}_2\text{O}_3, 4\text{K}_2\text{O} + 9\text{H}_2\text{O}$ ; with excess of chromate, the precipitate is orange-yellow, and has the composition  $9\text{CrO}_3, 2\text{Fe}_2\text{O}_3, 6\text{K}_2\text{O} + 6\text{H}_2\text{O}$ , if washed with alcohol, or  $10\text{H}_2\text{O}$  if washed with water; with only a slight excess of the ferric salt, the product is  $10\text{CrO}_3, 3\text{Fe}_2\text{O}_3, 6\text{K}_2\text{O} + 5\text{H}_2\text{O}$ . In hot solutions, the products, with all proportions, are complex mixtures.

Ferric chloride and potassium chromate yield ruby-red crystals of the compound  $7\text{CrO}_3, 2\text{Fe}_2\text{O}_3, 2\text{K}_2\text{O} + 7\text{H}_2\text{O}$ ; with a large excess of dichromate, the compound obtained by Hensgel in another way,  $4\text{CrO}_3, \text{Fe}_2\text{O}_3, \text{K}_2\text{O} + 4\text{H}_2\text{O}$ , is also formed; with excess of ferric chloride, potassium chlorochromate is one of the products. By diffusion of one solution into the other, an anhydrous crystallised chromate,  $6\text{CrO}_3, 2\text{Fe}_2\text{O}_3, 3\text{K}_2\text{O}$ , is obtained.

In hot solutions with large excess of dichromate, the so-called "jaune siderin" is obtained; it has the composition



Ferric chloride and ammonium dichromate in the cold yield Hensgel's chromate,  $4\text{CrO}_3, \text{Fe}_2\text{O}_3, (\text{NH}_4)_2\text{O} + 4\text{H}_2\text{O}$ , in red crystals.

C. H. B.

**Metallic Sulphides.** By A. VILLIERS (*Compt. rend.*, 1894, 119, 1208—1210).—It is well known that cobalt and nickel sulphides in

their ordinary form are insoluble in moderately concentrated hydrochloric acid, although the sulphides are not precipitated by hydrogen sulphide from slightly acidified aqueous solutions of nickel and cobalt salts of inorganic acids, whereas zinc sulphide is partially precipitated from acid solutions of zinc salts, although zinc sulphide is dissolved by dilute acids. The author considers that at the moment of their formation the cobalt and nickel sulphides are in a form more readily soluble in dilute acids than zinc sulphide, but in the absence of free acid they at once, and spontaneously, undergo a change analogous to that which takes place when chromic oxide and aluminium oxide are heated at a high temperature, and become in consequence insoluble in acids.

The author considers that this hypothesis explains the results obtained by Baubigny (Abstr., 1882, 805, 928, 1031, 1032, 1172), but is unable to accept Baubigny's view that the observed phenomena are due to the formation and subsequent decomposition of hydrosulphides of the sulphides.

It is probable that in neutral or feeble acid solutions of nickel and cobalt salts hydrogen sulphide produces, as in the case of zinc salts, an immediate, but very minute, precipitate, and this at once undergoes either a simple molecular condensation or a condensation accompanied by loss of water or hydrogen sulphide, and becomes insoluble in acids. Equilibrium is thus disturbed, and the separation of the sulphide continues slowly until a limit is reached which is independent of the degree of dilution of the free acid originally present. Even if zinc sulphide undergoes a similar change, it remains soluble in acids. (See also Baubigny, Abstr., 1888, 113.) C. H. B.

**Nickel and Cobalt Sulphides.** By A. VILLIERS (*Compt. rend.*, 1894, 119, 1263—1266).—Nickel sulphide only dissolves in ammonium or sodium sulphides or hydrosulphides in presence of air or an excess of sulphur. If, however, a nickel solution is mixed with excess of sodium hydroxide (not potassium hydroxide) to which has been added sufficient tartaric acid to prevent precipitation of nickel hydroxide, and the liquid is saturated with hydrogen sulphide, a black liquid is obtained without the formation of any precipitate. The tartaric acid simply prevents precipitation of nickel hydroxide, and if freshly precipitated hydroxide is immediately treated with hydrogen sulphide in presence of excess of sodium hydroxide, part of the nickel sulphide dissolves in the alkali sulphide. With an ammoniacal solution of nickel oxide, no similar phenomenon is observed, and the nickel sulphide dissolves only in presence of air. It is clear that nickel sulphide at the moment of its formation has properties different from those of the ordinary precipitated sulphide, and the difference is due to a molecular change which takes place very rapidly (preceding abstract).

If two equal volumes of a nickel solution are mixed with equal volumes (in excess) of sodium hydroxide, and saturated with hydrogen sulphide, in the one case rapidly and in the other slowly, the greater part of the nickel sulphide remains in solution in the former case, but is precipitated in the latter. If hydrogen sulphide is passed into a



boiling solution of a nickel salt, mixed with tartaric acid and excess of sodium hydroxide, only very little of the nickel sulphide remains in solution, the molecular change being much more rapid at the higher temperature. On the other hand, the black solution formed in the cold can be boiled for a long time without precipitation of the sulphide, but precipitation takes place immediately on the addition of a slight excess of acid.

Cobalt sulphide is insoluble in excess of alkali sulphides or hydro-sulphides, except in presence of a very large excess of sulphur, when traces of cobalt will dissolve. It follows that cobalt sulphide is either insoluble in alkali sulphides at the instant of its formation, or undergoes molecular change with much greater rapidity than nickel sulphide. The latter view seems to be correct, for with cobalt solutions containing not more than 3 or 4 parts of the salt in 100,000, the same phenomena are observed as with nickel, provided that too large an excess of sodium hydroxide is not added. C. H. B.

**Green Chromic Chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .** By AUGUSTO PICCINI (*L'Orosi*, 17, 329—334).—Silver nitrate at once precipitates two-thirds of the chlorine present in aqueous solutions of green chromium chloride; the remaining third is only precipitated very slowly. The author shows that silver fluoride immediately precipitates the whole of the chlorine present. Silver nitrate immediately precipitates the whole of the chlorine from solutions of green chromic chloride; in ethylic alcohol or acetone, as is shown by boiling point determinations, no electrolytic dissociation occurs. Methylic alcohol solutions of the green salt are intermediate in behaviour between aqueous and ethylic alcohol solutions, both in respect to the amount of chlorine which is immediately precipitable by silver nitrate, and the extent to which electrolytic dissociation occurs. In those cases in which all the chlorine is precipitated immediately by silver nitrate, the supernatant chromium solution remains green, whilst in those in which only a part separates at once as silver chloride, the solution gradually becomes violet. W. J. P.

**Complex Inorganic Acids.** By WOLCOTT GIBBS (*Amer. Chem. J.*, 1895, 17, 73—91; compare this Journal, 1877, ii, 847, and Abstr., 1886, 511).—*Platinotungstates*.—The best method for preparing these salts is by dissolving pure crystallised sodium tungstate in water, adding a large excess of soda, and then, gradually, a neutral solution of platinic chloride until a distinct excess of platinic hydroxide is present. Acetic acid is then added in slight excess. The following salts were obtained.

$10\text{WO}_3, \text{PtO}_2, 4\text{Na}_2\text{O} + 23 \text{ aq.} \dots$	Yellow crystals.
$10\text{WO}_3, \text{PtO}_2, 6\text{Na}_2\text{O} + 28 \text{ aq.} \dots$	Dull orange crystals.
$20\text{WO}_3, \text{PtO}_2, 9\text{Na}_2\text{O} + 58 \text{ aq.} \dots$	Topaz-yellow crystals.
$30\text{WO}_3, 2\text{PtO}_2, 15\text{Na}_2\text{O} + 89 \text{ aq.} \dots$	Dull yellowish crystals.
$30\text{WO}_3, \text{PtO}_2, 12\text{Na}_2\text{O} + 72 \text{ aq.} \dots$	Large, honey-yellow crystals.

Qualitative tests point to iridium, ruthenium, palladium, and osmium forming similar salts.

*Platinomolybdates*.—The following are described.

$8\text{MoO}_3, 2\text{PtO}_2, 3\text{Am}_2\text{O} + 12 \text{ aq.}$	.....	Lemon-yellow crystals.
$4\text{MoO}_3, 2\text{PtO}_2, 2\text{Am}_2\text{O} + 19 \text{ aq.}$	.....	Dark brown mass.
$60\text{MoO}_3, \text{PtO}_2, 10\text{K}_2\text{O} + 40 \text{ aq.}$	.....	Granular, yellow crystals.

In almost all these salts, the alkali may be replaced by other metals by double decomposition.

*Pyrophosphomolybdates* and *Pyrophosphotungstates*.—The following are described.

$22\text{MoO}_3, 2\text{P}_2\text{O}_5, 7\text{MnO}, 9\text{Na}_2\text{O} + 57 \text{ aq.}$	Bright yellow crystals.
$20\text{MoO}_3, 2\text{P}_2\text{O}_5, 10\text{MnO}, 5\text{Am}_2\text{O} + 10 \text{ aq.}$	Buff compound.
$14\text{WO}_3, \text{P}_2\text{O}_5, 3\text{MnO}, 6\text{Na}_2\text{O} + 36 \text{ aq.}$	.. Brownish-orange crystals.
$28\text{WO}_3, 2\text{P}_2\text{O}_5, 6\text{MnO}, 5\text{Am}_2\text{O}, 2\text{Na}_2\text{O} + 48 \text{ aq.}$	..... Orange prisms.

These salts are mostly soluble in boiling water.

L. T. T.

**Atomic Weight of Tungsten.** By MARY E. PENNINGTON and EDGAR F. SMITH (*Zeit. anorg. Chem.*, 1895, **8**, 198—204).—The authors are of opinion that the tungsten employed in former determinations of the atomic weight has not been free from molybdenum. They prepare their pure tungsten as follows:—Tungstic acid is heated for three days with concentrated nitric acid, and the yellow oxide washed with water and boiled several times with aqua regia and then with water until all the iron is extracted. The oxide is then dissolved in yellow ammonium sulphide, filtered, and the solution evaporated nearly to the point of crystallisation, and mixed with hydrochloric acid. The precipitate is ignited, extracted with nitric acid, and then with aqua regia, and dissolved in ammonia. The ammoniacal solution is treated with hydrogen sulphide, warmed for some hours at  $80^\circ$ , and then precipitated with pure, dilute hydrochloric acid. The trisulphide so obtained is heated in a porcelain crucible and converted into oxide. The product contains neither silica, iron, manganese, tin, nor tantalum, but it contains molybdenum. To eliminate the last impurity, it is heated at  $150$ — $200^\circ$  in a current of hydrogen chloride, whereby the molybdenum is sublimed as the compound  $\text{MoO}_3, 2\text{HCl}$ . The tungstic oxide is then dissolved in ammonia, crystallised three times, dried and ignited, and finally reduced by heating in a current of hydrogen. The product is greyish-black, and has the sp. gr. =  $18.64$  at  $0^\circ$ .

The atomic weight was determined by estimating the amount of oxygen absorbed in the conversion of the tungsten into tungstic oxide, namely, by heating the tungsten in a porcelain crucible exposed to the air until a constant weight was obtained.

The mean results obtained from a series of nine experiments was  $W = 184.921$ , taking  $O = 16$ .

E. C. R.

**Atomic Weight of Tungsten.** By EDGAR F. SMITH and EN. D. DESI (*Zeit. anorg. Chem.*, 1895, **8**, 205—206).—The pure tungstic oxide was prepared as described in the preceding abstract, and the determination of the atomic weight was effected by estimating the quantity of water formed during the reduction of tungstic oxide to

tungsten. The hydrogen employed in the experiments was prepared from pure zinc and sulphuric acid, and purified by passing through flasks containing potassium permanganate, alkaline lead nitrate, silver nitrate, potassium hydroxide, and sulphuric acid; it was then passed through calcium chloride, and finally through a heated tube, 23 cm. long, filled with clean iron wire. The water formed during the reduction was collected in a tube filled with calcium chloride.

The mean result obtained from a series of six experiments was  
 $W = 184.704$ . E. C. R.

**Pyroantimonious acid.** By C. SERONO (*Gazzetta*, 1894, **24**, 274—276, and *J. pr. Chem.*, 1895, [2], **51**, 97—99).—The substance described by Schaffner (*Annalen*, 1844, **51**, 182) as pyroantimonious acid,  $H_4Sb_2O_6$ , is stated by him to be formed when antimony trisulphide is heated with aqueous potash, and copper sulphate then added. The author finds that the substance obtained by this method is orthoantimonic acid,  $H_2SbO_4$ , which is formed at the expense of a portion of the oxygen of the cupric salt, a cuprous salt being found among the products of the reaction. A. H.

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## Physiological Chemistry.

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**Blood Gases of Brain and Muscle in Rest and Activity.** By LEONARD HILL and D. N. NABARRO (*Proc. Physiol. Soc.*, 1895, 20—23).—The metabolism of resting muscles, as measured by the gaseous exchange, is very much greater than that of the resting brain. The venous blood leaving the two situations is different in colour, but this rough test is supported, in the present case, by careful and numerous analyses of the blood gases. The metabolism in muscles in the state of activity is enormously increased. The metabolism in the brain during an epileptic fit induced by absinthe is somewhat, but not constantly, increased. This last point requires still further investigation. W. D. H.

**Gaseous Exchanges in Isolated Muscle.** By J. TISSOT (*Compt. rend.*, 1895, 120, 568—570).—It was Hermann who first pointed out that the absorption of oxygen and production of carbonic anhydride in muscle are two distinct phenomena. The two experiments here recorded, in which isolated frog's muscles were employed, are stated to support this doctrine. The amount of oxygen absorbed and carbonic anhydride eliminated, were, however, estimated in different muscles at various temperatures. The amount of carbonic anhydride formed rises with the temperature, even after such heat has been applied as to kill the muscle. It is therefore not a measure of physiological activity. The amount of oxygen absorbed, on the other hand, reaches a maximum at from 33°—37°, a temperature at which the muscle is most active, and then falls. W. D. H.

**Regulation of Heat Production.** By MARCUS S. PEMBREY (*Proc. Physiol. Soc.*, 1895, 3—4).—Experiments made on mice show that they respond to changes of external temperature like cold-blooded animals if they are anaesthetised, or after section of the spinal cord. The section of the cord must be made sufficiently high up, so that they are no longer able, by the activity of the few muscles over which they still have control, to keep up the temperature of their tissues.

W. D. H.

**The Minimum Amount of Nitrogen required by Human Beings.** By LOUIS LAPICQUE and CH. MARETTE (*Compt. rend. Soc. Biol.*, 1894, 273—275).—Two experiments are recorded; in both, the daily ration of albumin was 57 grams. In the first case, where the experiment lasted 10 days, the excreta contained 9.15 grams of nitrogen, corresponding with 58.5 grams of albumin. There was thus a daily deficit of 1.5 grams of albumin, and a loss of body weight in the 10 days of 500 grams. In the second case, the experiment lasted eight days, the body weight did not change, and the daily excretion of nitrogen was 8.28 grams, corresponding with 53.7 grams of albumin, or a daily assimilation of 3.4 grams of albumin. The conclusion drawn is that a little more than 7 grams of nitrogen *per diem* is about enough to maintain nitrogenous equilibrium.

W. D. H.

**Peptic Digestion.** By FERDINAND KLUG (*Pflüger's Archiv*, 1895, 60, 43—70).—The following are the results of this investigation. Successive extracts of the same mucous membrane possess different activities, the later being more active than the earlier ones. The activity of the first extract is, however, increased by dilution with weak hydrochloric acid, or by allowing it to digest itself for 24 hours. For experiments on artificial digestion, boiled white of egg is recommended as the best; this, however, already contains about 0.7 per cent. of deuterio-albumose. Ammonium sulphate and sodium chloride retard the course of the digestion: the latter, if present to a greater extent than 0.5 per cent.

The quantity of pepsin has an important influence; the best is from 0.5 to 0.01 per cent. of the pepsin solution. With greater or less concentrations, the activity lessens; still, digestion does occur with a pepsin percentage of 0.005. Dog's pepsin, with a concentration of 0.01 per cent., is more active than pig's or ox pepsin similarly diluted; the optimum percentage for these two animals is 0.1

The optimum percentage of hydrochloric acid is 0.5 to 0.6. Gastric juice with less than 0.1 per cent. of hydrochloric acid does not act on white of egg. The best artificial juice therefore contains 0.1 per cent. of pepsin and 0.6 per cent. of hydrochloric acid. Twenty c.c. of such a juice will dissolve 6 grams of hard-boiled white of egg within 10—15 hours. Digestion proceeds most rapidly in the first four hours. Syntonin and albumoses appear five minutes after the commencement of the digestion. Peptone makes its appearance with dog's pepsin in 20—40 minutes, with the pepsin of ox and pig in four hours. Dog's pepsin also forms more peptone in the same time than the other pepsin. It is even suggested that different pepsins exist.

Digestion ceases at  $0^{\circ}$ ; it increases with the temperature, reaching its maximum between  $50^{\circ}$  and  $60^{\circ}$ ; it then becomes less active, and ceases entirely at  $80^{\circ}$ . Syntonin and albumoses appear simultaneously; syntonin, however, is not regarded merely as a product of the hydrochloric acid, but, like albumoses and peptone, is the result of the activity of pepsin hydrochloric acid. The paper is illustrated by charts and tables. In the estimation of peptone, the spectrophotometer applied to the biuret reaction was found to give good results.

W. D. H.

**Pancreatic Digestive Products of Albumin.** By MARCELLUS NENCKI (*Ber.*, 1895, 28, 560—567).—Finely divided pancreas was treated with water and a little chloroform at the ordinary temperature for three days; the liquid was boiled, the coagulated albumin separated, and the cold filtrate treated with mercuric chloride. Xanthine, guanine, hypoxanthine, and adenine-hypoxanthine were isolated from the precipitate. It has been previously shown that with picric acid instead of mercuric chloride, glutine and pentamethylenediamine picrates are deposited. The filtrate from the mercuric chloride precipitate, when concentrated, deposits tyrosine, and then, by the cautious addition of bromine water, proteinochromogen, which, although apparently homogeneous, consists of at least two substances which could not be completely separated; one of these is red, contains Br 27, S 0.5 per cent., the other is brown, and contains Br 20.5, S 2.2 per cent. The former, in alcoholic solution, shows a characteristic absorption band in the green. When fused with potash, the bromine compound yields scatole, pyrroline, and indole. Attention is drawn to the similarity between the bromine derivatives and other animal pigments, both in composition (calculated as free from bromine) and in the decomposition products. This being the author's first communication on proteinochromogen, the statement in the German edition of Halliburton's text-book of chemical physiology, that he has previously alleged this compound to be a naphthylamine, is incorrect.

J. B. T.

**Glycogen in the Blood.** By MAURICE KAUFMANN (*Compt. rend.*, 1895, 120, 567—568).—The statement of Salomon, Huppert, and Czerni is confirmed that glycogen is a constituent of normal blood. The blood of horse, ox, and dog was examined. The blood of animals rendered diabetic by extirpation of the pancreas contains much more glycogen than that of normal animals; in some cases, 20 times as much, namely, 500 milligrams instead of 25 milligrams per litre. This explains the accumulation of glycogen which has been noted in the capillary network and tissues of the nerve centres and kidney, and the presence of glycogen in the urine, which facts have been noted in diabetic patients.

W. D. H.

**Sugar and Muscular Work.** By JOSEF SEEGEN (*Chem. Centr.*, 1894, ii, 795; from *Centr. Physiol.*, 8, 417—422).—The work of Chauveau and Kaufmann on this subject is criticised. Their conclusions rest chiefly on analyses of the arterial and venous blood of muscle; but the differences in the amount of sugar between the two, both for

resting and active muscle, are stated to be so small as to come completely within the limits of experimental error. Further, if the source of muscular energy is sugar, one arrives at curious arithmetical results, like the following :—A dog weighing 40 kilos., and containing 16 kilos. of muscular tissue, would need, in the 24 hours, 840 grams of sugar if at rest, 3230·4 grams of sugar if doing work ; in order to obtain this from meat, the resting dog would have to take 2·12 kilos., and the working dog 9·7 kilos. daily.

W. D. H.

**Oxidising Action of Animal Tissue.** By FRANZ RÖHMANN and WILHELM SPITZER (*Ber.*, 1895, **28**, 567—572).—The oxidation of stable substances such as fats, carbohydrates, &c., in the body, has been compared by Hoppe-Seyler to the action of palladium hydrogenium, the nascent hydrogen decomposing an oxygen molecule and combining with 1 atom, whilst the second attacks the oxidisable compound. M. Traube dissents from this view, and considers that the tissues act in a similar manner to certain finely-divided metals or salts, which undergo no apparent change but are able to cause the evolution of oxygen from many compounds that contain it. If this theory is correct, certain dyes, which are only slowly acted on by air, should be much more readily oxidised when treated with animal tissue.  $\alpha$ -Naphthol and paraphenylenediamine, or dimethylparaphenylenediamine, in dilute alkaline solution, metatolylenediamine, and paraphenylenediamine, or dimethylparaphenylenediamine, dimethylparaphenylenediamine, and dimethylaniline, readily oxidise when treated with fresh well washed liver. The reaction may be easily shown by dipping a paper into the mixed solutions and rubbing with the liver ; wherever this is placed, the colour is developed. The liver must be taken from an animal recently killed ; if it is then finely-divided and treated with alcohol and ether, it retains its activity for an indefinite period. The active substance is unknown, but is a characteristic constituent of the cells, W. Spitzer having shown that dextrose is rapidly oxidised both by red and white corpuscles, whilst blood-serum is without action. A strongly reducing substance is also present which is not decomposed by boiling, and is, therefore, not identical with the oxygen carrier, as Hoppe-Seyler supposes ; its presence is necessary for the production of the above colours, as tissue from animals dead some time is unable to induce oxidation.

J. B. T.

**Fibrinogen and Fibrin.** By MAURICE ARTHUS (*Compt. rend. Soc. Biol.*, 1894, 306—309).—It is found that the weight of fibrin produced in oxalated plasma by adding a calcium salt is less than the weight of fibrinogen obtained by weighing the heat coagulum at 56°, and therefore considerably less than the total quantity of fibrinogen, which does not all come down at 56°, as Hammarsten first showed. Hence, in the formation of fibrin from fibrinogen there must be a decomposition of the latter.

W. D. H.

**Fibrinogen and Fibrin.** By GEORGES HAYEM (*Compt. rend. Soc. Biol.*, 1894, 309—310).—In reference to Arthus' work (see preceding abstract), it is pointed out that fibrinogen is not a well characterised

substance, and that perhaps varieties exist. For instance, with plasma, the amount of fibrinogen depends on the manner in which decantation is performed and heat is applied. In lymph, the quantity of fibrinogen coagulated at  $56^{\circ}$  is notably less than that of fibrin. In inflammatory dropsical fluids, the difference is greater but in the same direction. In transudations which are not spontaneously coagulable, although heating to  $56^{\circ}$  destroys their power of coagulating on the addition of serum, it is stated to produce no coagulum of fibrinogen.

W. D. H.

**Coagulation of Fibrinogen.** By EDWARD A. SCHÄFER (*Proc. physiol. Soc.*, 1895, 18—20).—Lilienfeld (this vol., ii, 52), states that if fibrinogen is prepared pure by Hammarsten's method and dissolved in dilute sodium chloride solution, the addition of acetic acid produces a precipitate; this he terms thrombosin; after washing with water the precipitate is dissolved in a little sodium carbonate solution; the addition of calcium chloride to this produces a coagulum of fibrin.

In the present research, it is shown that in this respect fibrinogen resembles thrombosin in spite of Lilienfeld's assertion to the contrary, and, therefore, further evidence is necessary that thrombosin and fibrinogen are different substances.

Further, Lilienfeld does not prove that nucleo-albumin does not enter into the reaction; for it is impossible to prepare a fibrinogen which does not leave a residue on gastric digestion. The fibrin prepared from such pure fibrinogen leaves a similar residue. Lilienfeld asserts that fibrinogen may itself be a nucleo-albumin, but the amount of residue is small, and it is more probable that the source of the phosphorus-containing digestion residue is nucleo-albumin, which has clung to the fibrinogen, and its presence explains the fact that addition of calcium chloride is all that is necessary for fibrin formation.

Blood plasma slowly coagulates, yielding fibrin even when oxalated; if it is assumed that calcium is a necessary component of fibrin, we must conclude that fibrinogen can slowly take it up even in the presence of soluble oxalates.

W. D. H.

**Physiological Action of Extract of Suprarenal Capsules.** By GEORGE OLIVER and EDWARD A. SCHÄFER (*Proc. Physiol. Soc.*, 1895, 9—14).—An aqueous, dilute alcoholic, or glycerol extract of suprarenal capsules, when intravenously injected in small quantities into dogs or rabbits, produces (1) an extreme contraction of the arteries; (2) a rise of arterial pressure in spite of cardiac inhibition, but which is increased by section of the vagi; (3) central vagus stimulation leading to standstill of the auricles, although the ventricles continue to contract with a slow independent rhythm; (4) acceleration and augmentation of the heart's beat, best marked in the auricles after section of the vagi; (5) respiration is slightly shallower. The effects last while the injection lasts, but do not produce death in dogs. The peripheral constriction of the arteries is shown by the plethysmograph applied to the limbs, or the oncometer applied to the kidney. Stimulation of the depressor nerve fails to produce its usual result while the injection lasts. On the isolated frog's heart, solu-



tions of 5 per cent. are necessary to produce results. The effect on voluntary muscles is not marked, but on electrical stimulation through their nerves there is delay in relaxation. It is considered probable that the active material is taken up by and stored within the muscles. The toxic properties are possessed by the medulla not by the cortex of the suprarenal capsules. The suprarenals of man act similarly except in cases of Addison's disease, where they give an entirely negative result. Gastric digestion does not impair the activity of the extract.

The evidence obtained leads to the view that the suprarenal bodies are secretory rather than destructive, and the secreted product is in all probability of great physiological importance for maintaining the tonicity of the muscular tissues in general, and especially of the heart and arteries.

W. D. H.

**The Physiologically Active Substance occurring in the Suprarenal Gland.** By B. MOORE (*Proc. Physiol. Soc.*, 1895, 14—17).—This substance is probably a powerfully reducing material found only in the medulla of the gland, and first described by Vulpian. It gives a dark green or blue colour with ferric chloride, passing through purple to a dark red on the addition of ammonia or sodium carbonate. With chlorine, bromine, or iodine water, peroxide of hydrogen or alkalis in the presence of oxygen, it gives a rose-red coloration discharged by sulphide of hydrogen or ammonium.

It is insoluble in organic solvents like alcohol, ether, or benzene; it is soluble in water and dilute acids. It is found only in the suprarenal capsule, or after death in the blood of the suprarenal vein. Its presence in physiologically active extracts was constant; when absent, the extracts gave a negative physiological result.

It has not yet been separated, and its characters are largely negative; it has not been identified. It is not attacked by acids, or by boiling for some minutes, but it is destroyed by alkalis, by oxidising agents and by prolonged boiling. It is not precipitated by alcohol, saturation with ammonium sulphate, by mercuric chloride, potassio-mercuric iodide, or tannic acid. It does not reduce Fehling's solution, even after boiling with mineral acids, nor does it form a crystalline compound with phenylhydrazine. It is not volatile either alone or with aqueous vapour. It dialyses freely through parchment paper, and the highly active dialysate is free from proteids.

W. D. H.

**Proteids of Suprarenal Capsules.** By D. N. NABARRO (*Proc. Physiol. Soc.*, 1895, 17—18).—The proteids dissolved out by 5 per cent. solutions of magnesium sulphate are chiefly globulins and nucleo-albumins. Pepsin and peptone are absent, and albumin is only present in small quantities.

W. D. H.

**Urea in Arterial and Venous Blood.** By MAURICE KAUFMAN N (*Compt. rend. Soc. Biol.*, 1894, 93—95).—By experiments on horses and dogs, using Gréhan's method of estimation, it is found that the percentage of urea in arterial and venous blood is practically the same. The small differences noted come within the limits

of experimental error. If differences exist, they would be expected to be very small; these experiments should not lead to the conclusion that no urea is formed in limbs or head. W. D. H.

### Absorption and Elimination of Glycero-phosphoric acid.

By GUISTO PASQUALIS (*Chem. Centr.*, 1894, ii, 709; from *Annali Chim. Farm.*, 20, 145—154).—Calcium glycero-phosphate is easily digested and passes quickly into the circulation. Normal calcium phosphate is digested but with greater difficulty, and goes more slowly into the circulation. Glycero-phosphoric acid passes at least in greatest part as such into the blood and is excreted in the urine as phosphoric acid; the decomposition of glycero-phosphoric acid into glycerol and orthophosphoric acid must occur in some one organ. Glycero-phosphoric acid is regarded as of great therapeutic and physiological value. W. D. H.

**Saturation of Normal Urine with Neutral Salts.** By ARTHUR EDMUNDS (*J. physiol. Chem.*, 1895, 17, 451—454).—Saturation of horse's or human urine with ammonium sulphate causes a precipitation of ammonium urate. The precipitate comes down less rapidly than that caused by ammonium chloride. The precipitate is tinged pink, and is mixed with some calcium sulphate. Saturation of human urine with magnesium sulphate also causes a small precipitate which is tinged with urobilin, but is chiefly inorganic in nature, consisting of calcium sulphate and magnesium phosphate. After saturation with this salt, the urine no longer gives the tests for calcium. With horse's urine, the precipitate produced by saturation with magnesium sulphate is more abundant, and differs from that obtained from human urine in containing very little phosphate, but abundance of carbonate of magnesium. Horse's urine is very poor in phosphates.

The mere appearance of a precipitate on saturating urine with these salts does not, therefore, indicate the presence of proteid, and may constitute a source of error in the quantitative estimation of the varieties of proteid (albumin and globulin) present in cases of albuminuria. Noël Paton's latest method, however, does not introduce this error; the total proteid is estimated by weighing the heat coagulum; another specimen is half saturated with ammonium sulphate to precipitate globulin; the albumin is estimated by weighing the heat coagulum in the filtrate, and the amount of globulin is obtained by difference. Half saturation of normal urine by ammonium sulphate causes no precipitate in normal urine. Saturation of normal urine with sodium chloride or sodium sulphate produces no precipitate.

W. D. H.

### Toxicological Investigation of Potassium Silicate.

By P. LAGUARDIA (*L'Orosi*, 17, 217—224).—From experiments made on rabbits, the author finds that a dose of 1—2 grams is toxic, the substance acting like caustic poisons such as the alkali oxides, hydroxides, and carbonates; an examination of the liver, bile, and urine, shows that the silicate is not absorbed by the system. In cases of poisoning by potassium silicate, the chemical examination, a complete scheme

for which is given in the paper, should be made on the stomach and its contents, the intestines, the vomit, and the fæces. W. J. P.

### Physiological Action of Acetonitrile and its Homologues.

By S. LANG (*Chem. Centr.*, 1894, ii, 796; from *Arch. exp. Path. Pharm.*, **34**, 247—258).—After feeding a dog, weighing 18 kilos., with from 0.5 to 9 c.c. of acetonitrile mixed with its food, the urine gave a red colour on the addition of ferric chloride. This depends not exclusively on the presence of acetic acid, but is also due to ammonium thiocyanate. Toxic symptoms (vomiting) were only observed when more than 5 c.c. of acetonitrile was given. The same applies to rabbit's urine. There must therefore be a separation of the two carbon atoms, and the CN-group so split off unites with the group SH. The  $\text{CH}_3$ -group appears in the urine as formic acid. Propionitrile, butyronitrile, and capronitrile lead constantly to the appearance of thiocyanate in the urine; the corresponding fatty acid was not found; the organism probably exercises a greater power of oxidising ethyl, propyl, and butyl groups than it possesses over methyl.

W. D. H.

### Change of Cyanogen Compounds in the Body.

By W. PASCHELES (*Chem. Centr.*, 1894, ii, 797; from *Arch. exp. Path. Pharm.*, **34**, 281—288).—The work of Lang (see preceding abstract) led to the present investigation, which relates to the action of living tissues on cyanogen compounds. Sodium cyanide was mixed with the freshly-removed tissues and organs; it was found that both muscle and ox liver possess the power of decomposing a portion of the cyanide, especially the liver, particularly at the body temperature. By union with sulphur, thiocyanate is formed. The same occurs with albumin, the loosely combined sulphur playing an important part in the reaction. Alkali albumin contains no loosely combined sulphur, acid albumin does; the latter reacts with cyanides in the manner described, the former does not. Cystin can also change cyanogen into thiocyanate.

W. D. H.

### Physiological Action of Chlorocaffeine and Cyanocaffeine.

By JOHN W. PICKERING (*J. Physiol.*, 1895, **17**, 395—401).—The introduction of an atom of chlorine into the caffeine molecule considerably modifies its physiological action, as tested on the hearts of embryo chicks, frogs, and human beings. It appears that a chemical stimulus or depressant may exert its action, due to one or more molecular groups in its substance; and that one group of atoms may modify the physiological action of other groups of atoms in the same molecule. This apparently occurs in the case of chlorocaffeine, the three methyl groups would tend to induce tonic contraction of the heart muscle, and the chlorine atom to produce an atonic condition. Chlorocaffeine (chlorotrimethylxanthine) produces far less tonic contraction of the heart than caffeine itself. Thus here is a case of physiological antagonism going on in the interaction of the parts of one molecule and living contractile tissue.

In the introduction of cyanogen into the caffeine molecule, the cyanogen overpowers the physiological action of the three methyl

groups, and the cyanocaffeine acts more like a cyanogen derivative than a xanthine derivative, being almost immediately fatal to the heart of chick and frog; there is no evidence of tonic contraction at all, and the heart dies in extreme diastole.

The possibility of the living tissue decomposing the chlorocaffeine and cyanocaffeine into free chlorine, cyanogen, and caffeine respectively was not overlooked, but tests failed to give evidence of these substances.

A solution of caffeine in 'chlorine water acts differently, the free chlorine being very toxic to the heart. Chlorocaffeine is a powerful diuretic and apparently also a cerebral stimulant. W. D. H.

**Influence of Saline Media on Tadpoles.** By SYDNEY RINGER and ARTHUR G. PHEAR (*J. Physiol.*, 1895, **17**, 423—432).—Distilled water kills tadpoles in from 2—6 hours; paralysis is quickly followed by disintegration; indeed signs of desquamation may be observed before movement has entirely ceased. Certain salts when added in minute quantities such as occur in river water, sustain motion in some cases for many days. Some of these sustaining salts are, however, poisons, such as hydrocyanic acid, potassium cyanide, and normal potassium oxalate.

Carbonates, citrates, and tartrates also sustain life. A solution of 0.00025 per cent. of potassium ferrocyanide will sustain life for six days. Sodium sulphate, phosphate, sulphite, and arsenate, and ammonium oxalate are not so efficacious, but are superior to distilled water. Potassium chloride, sulphate, nitrate, chlorate, acetate, oxalate ( $\text{KHC}_2\text{O}_4$ ) and phosphate, sodium acetate, and calcium chloride and sulphate kill as soon as or sooner than distilled water. Extremely dilute acids and alkalis sustain life also. A large number were tried; the dilution in the cases of hydrochloric, sulphuric, and hydrocyanic acids were 1 to 70,000, 200,000, 500,000 respectively. The explanation advanced is that the salt or acid acts not by being absorbed in appreciable doses, especially in the case of poisons, but merely by maintaining the integrity of the cuticle, and preventing the disintegration which is the cause of death produced by distilled water. On increasing the dose beyond a certain limit, the poisonous action of the salt asserts itself. W. D. H.

**Influence of Saline Media on Tubifex Rivulorum.** By SYDNEY RINGER and ARTHUR G. PHEAR (*Proc. Physiol. Soc.*, 1895, 23—27).—A similar investigation with similar results to that recorded in the foregoing research on tadpoles. W. D. H.

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### **Chemistry of Vegetable Physiology and Agriculture.**

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**Detection of Hydrogen Peroxide in Green Plants.** By A. BACH (*Compt. rend.*, 1894, **119**, 1218—1221).—Perchromic acid in ethereal solution containing a free acid, readily converts aniline into

a violet colouring matter, and hence a very dilute solution of potassium dichromate, mixed with aniline and a free acid, can be used for the detection of hydrogen peroxide.

The best results are obtained with a solution containing 0.03 gram of potassium dichromate and 5 drops of aniline per litre.

Experiments with different acids in various proportions show that oxalic acid gives the most rapid and distinct results. Since potassium dichromate in presence of a free acid slowly oxidises aniline, even when no hydrogen peroxide is present, it was necessary to determine the conditions which enable the one action to be distinguished from the other. The action of oxalic acid on the reagent is considerably retarded by dilution; 4 drops of a 5 per cent. solution of the acid, added to 5 c.c. of the reagent, gave a coloration after about an hour, but if the reagent was previously diluted with an equal volume of water the coloration did not appear until after 15 hours. The rate of action of the oxalic acid also decreases as the proportion added is reduced; 20 drops of the 5 per cent. solution, added to 5 c.c. of the reagent, diluted with an equal volume of water, gave a coloration after 12 minutes; whilst with 2 drops, 36 hours was necessary, and with 1 drop, 78 hours. In presence of hydrogen peroxide, 1 drop of the acid solution produces a coloration in from 10 to 30 minutes, and there is therefore a sufficiently wide margin between the two reactions.

In practice, 5 c.c. of the dichromate and aniline solution is mixed with 5 c.c. of the liquid to be tested, and 1 drop of the 5 per cent. solution of oxalic acid. A blank experiment may be made at the same time.

Nitrous acid and nitrogen oxides are without action on the reagent, but the coloration is produced by hypochlorous acid and hypochlorites, and by chlorine and chlorine oxides; but of a large number of non-oxidising substances examined, tannin alone was found to reduce the sensitiveness of the reagent.

Twenty-five grams of the leaves collected in the middle of the day are moistened with 75 c.c. of water containing 1 gram of oxalic acid per litre, the vessel being kept in the dark. Five c.c. of the liquid is withdrawn from time to time, and tested in the manner described.

Experiments made during October showed the presence of hydrogen peroxide in the following 18 plants:—*Brassica asperifolia*, *B. oleifera*, *Daucus carota*, *Beta vulgaris*, *Geranium rotundifolium*, *Hedera helix*, *Cerasus laurocerasus*, *Aster*, *Tropæolum pentaphyllum*, *Chrysanthemum balsamica*, *Mercurialis annua*, *Urtica*, *Caltha palustris*, *Vicia faba*, *Papaver rhæas*, *Sisymbrium nasturtium*, *Dianthus caryophyllus*, *Apium petroselinum*, *Fragaria vesca*. *Lactuca sativa*, and *Vicia* gave doubtful results, and *Medicago sativa*, *Chicorium intybus*, *Avena sativa*, *Viola odorata*, and *Lilium bulbiferum* gave negative results (compare this vol., ii, 26).

C. H. B.

**Atmospheric Ozone.** By J. PEYROU (*Compt. rend.*, 1894, **119**, 1206—1208).—Experiments were made during the months of July, August, September, and October with a view to ascertain what influence is exerted by vegetation on the proportion of ozone present in

the atmosphere. Iodised starch paper was exposed at a height of 0·5 metre above the surface of the soil in an arable field in fallow, and in an adjacent field with a vigorous crop of lucern, the two stations being 200 metres apart. In 172 cases out of 197, the paper placed above the growing crop indicated more ozone than the paper above the fallow, the differences in some instances being considerable; in 14 cases, both papers gave the same results, but on these days there was a dry wind unfavourable to vegetation; in 11 cases, the paper above the fallow indicated more ozone than that above the crop. Similar experiments, in which one paper was placed above bare soil and another over a young crop of radishes, gave similar results; in 22 cases, the paper over the growing crop indicated more ozone than that over the bare soil, whilst only in two instances was the reverse the case, and then there was a high wind. Confirmatory evidence was obtained in a greenhouse, more ozone being indicated in the immediate neighbourhood of plants than elsewhere. Any condition, such as the proximity of decomposing organic matter, which tends to destroy ozone, reduces the indications of the paper.

The quantity of ozone present is greater, the greater the activity of the surrounding vegetation, and this agrees with Houzeau's observation that the proportion of atmospheric ozone is highest in spring. The author has previously shown that there are two periods in the day when plants show a maximum absorption of oxygen (Abstr., 1889, 641—642). Observations made every two hours during 15 days in August, show that during the day the proportion of ozone is practically constant, but in the evening, from 6 to 9 p.m., there is, as a rule, little or no ozone in the atmosphere. Other experiments showed that, as a rule, the proportions of ozone in a large park containing a number of fir trees and in a garden in the open country were practically identical, whilst there was a higher proportion over a field near the park. These latter results do not agree with some early observations of Cloez.

Throughout the experiments from July to October, ozone was always recognisable in the air of the country during both day and night; but in Paris, even in the neighbourhood of trees, ozone was only recognisable during October when there were high winds.

C. H. B.

*Note by Abstractor.*—It seems not improbable that the results ascribed by the author to ozone are really due to hydrogen peroxide. (See Bach, Abstr., 1894, ii, 186—187, and this vol., ii, 26.)

**Chemical Composition of Kola-nut.** By C. UFFELMANN and A. BÖMER (*Zeit. angew. Chem.*, 1894, 710—713).—The authors have fully analysed 12 varieties of kola-nut, and tabulated the results.

The caffeine was estimated by boiling with water containing 5 per cent. of sulphuric acid, and further treating according to Mulder's directions. The starch was estimated by first boiling under pressure and then inverting. The ethereal extract, containing a little caffeine, was obtained by six or eight hours' extraction of the finely-powdered substance. The tannic acid was estimated by boiling

5 grams with 200 c.c. of water for one hour ; the liquid was then diluted to 500 c.c., and, in 200 c.c. of the filtrate, the acid was estimated by Fleck's method. Ready-formed sugar was only present in traces.

L. DE K.

**Phosphate from Grand-Connétable.** By AMBROISE ANDOUARD (*Compt. rend.*, 1894, **119**, 1011).—The phosphate from Grand-Connétable, an islet to the east of Cayenne, is amorphous, light, and very porous, and has a reddish-yellow to deep brick-red colour. It has the composition  $P_2O_5$ , 39.10;  $SiO_2$ , 1.70;  $SO_3$ , 0.06;  $CO_2$ , traces; Cl, traces;  $Al_2O_3$ , 25.59;  $Fe_2O_3$ , 8.03; CaO, 1.46; MgO, traces;  $H_2O$  (at  $105^\circ$ ), 21.24;  $H_2O$  (at a red heat), 2.50; residue, 0.38 = 100.00. The water is chiefly in a state of combination; determinations of hygroscopic moisture should be made somewhat below  $100^\circ$ .

The phosphate is insoluble in cold water, but is very soluble in acids and in a solution of ammonium citrate, and hence is readily assimilable. It has a rapid effect on crops, and may find useful employment in agriculture, although at present it is chiefly used for the manufacture of alum.

C. H. B.

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## Analytical Chemistry.

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**Simple Apparatus for Gas Analyses.** By CARL KIPPENBERGER (*Zeit. angew. Chem.*, 1894, 714—715).—The author has described an apparatus (*Abstr.*, 1894, ii, 477) for the measurement of gases. In using it, the gas to be measured must be expelled from the generating flask by means of water or else by means of another gas soluble in the liquid with which the apparatus is charged. The apparatus may, however, also be used in the analysis of pyrolusite or bleaching powder by simply decomposing these in the generating flask with hydrogen peroxide and noticing the amount of water displaced. The manipulation which becomes, of course, slightly different will be easily understood by those using the apparatus. L. DE K.

**Litmus and Methyl-orange as Indicators.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1894, 733—738).—Reinitzer (*this vol.*, ii, 134) has attempted to prove the superiority of litmus over methyl-orange in volumetric analysis. The author admits that in very dilute solutions litmus may prove the more delicate indicator, but, in ordinary practice, the results are almost identical. L. DE K.

**Detection and Estimation of Chlorine in presence of Iodine.** By P. N. RAIKOW (*Chem. Zeit.*, 1894, 18, 1661).—Phenylhydrazine is dissolved in dilute sulphuric acid and mixed with an excess of copper sulphate. If sufficient acid is present, the mixture will remain clear. Added to a soluble chloride containing an iodide, the latter causes a bulky, brownish precipitate containing all the iodine. Chlorine may then be tested for in the filtrate by adding silver sulphate.

The precipitate will yield its iodine to boiling aqueous potash, which may then be qualitatively or quantitatively estimated as usual.

Bromides also give a precipitate with the reagent, but too soluble to admit of quantitative estimation. It cannot, however, be separated from the iodine compound by simple washing. L. DE K.

**Estimation of Nitrogen in Feeding Stuffs by Kjeldahl's Process.** By GERLACH and SÜVERN (*Chem. Zeit.*, 1894, 18, 1902—1903).—It has been mentioned of late that when applying Kjeldahl's process to the analysis of cotton-seed meal, a two or three hours' boiling with sulphuric acid and mercury is insufficient to convert all the nitrogen into ammonia, but that addition of phosphoric anhydride will hasten the operation.

The authors having made a large number of experiments conclude that there is no necessity for adding any phosphoric anhydride, and that two or three hours' boiling is amply sufficient. L. DE K.

**Estimation of Nitrogen in Nitro-cellulose, &c.** By DUSCHAN STANOJEWITSCH (*Zeit. angew. Chem.*, 1894, 676—678).—The apparatus used by the author is a combination of Schloesing's apparatus with Lunge's nitrometer. The substance to be tested is introduced into the decomposing flask containing 50—60 grams of mercury, and the air is then expelled from the flask by means of a current of carbonic anhydride, which is in turn absorbed by having the nitrometer filled with aqueous soda. Finally, sulphuric acid is admitted into the flask, and the liberated nitric oxide collected and measured in the nitrometer, the last traces being expelled from the flask by a current of carbonic anhydride. L. DE K.

**Estimation of Nitrogen and Phosphoric acid.** By HUGO NEUBAUER (*Zeit. angew. Chem.*, 1894, 678—679).—The author recommends the following process:—Ten grams of the manure is dissolved in a 500-c.c. flask, in 50—60 c.c. of sulphuric acid; 2 grams of mercury and a little paraffin are added, and the mixture boiled until colourless. After cooling, the liquid is diluted with water up to the mark; 1 c.c. of brine is added, and the whole is then filtered. Fifty c.c. of the filtrate is then used for the estimation of the phosphoric acid by the citrate method, and in another 50 c.c. the ammonia is estimated.

The phosphatic precipitate is practically free from mercury, and, therefore, does not, on ignition, give off any poisonous fumes.

L. DE K.

**Estimation of Citrate-soluble Phosphoric acid in Basic Slag and Mineral Phosphates.** By PAUL WAGNER (*Chem. Zeit.*, 1894, 18, 1153—1154).—The following reagents are required. (A) A solution of ammonium citrate, containing 160 grams of citric acid and 28 grams of nitrogen per litre; (B) a solution containing 150 grams of citric acid and 23 grams of nitrogen per litre; (C) a molybdenum solution, made by dissolving 125 grams of molybdic acid in a sufficiency of 2.5 per cent. ammonia, and, after adding 400 grams of ammonium nitrate, diluting to 1 litre. The solution

is then poured into 1 litre of nitric acid (sp. gr. 1.19), and, after standing for 24 hours at 35°, it is filtered.

**1st Method.**—(a) *Estimation of the Alkalinity of the Sample.*—Five grams of phosphate flour is put into a 500-c.c. flask, and this is filled up to the mark with a 1 per cent. solution of citric acid. After shaking for half an hour in a shaking apparatus, 50 c.c. of the filtered liquid is titrated with N/4 sodium hydroxide, using phenolphthaleïn as indicator, and the alkalinity of the sample is then found by a simple calculation. (b) *Estimation of Citrate-soluble Phosphoric acid.*—Five grams of the phosphate flour is put into a 500-c.c. flask, and mixed with 200 c.c. of water. After first adding sufficient 5 per cent. citric acid solution to neutralise the alkalinity, 200 c.c. of ammonium citrate (A) is added, and then water up to the mark. After shaking for half an hour, the liquid is filtered, and 50 c.c. of the filtrate is mixed with 100 c.c. molybdate solution (C), heated to 80°, and treated as usual.

**2nd Method.**—The alkalinity need not be estimated, but the sample is treated with 200 c.c. of water and 200 c.c. of ammonium citrate (B). After adding water up to the mark, the operation is conducted as before. There is not much to choose between the two processes.

L. DE K.

**Kalman and Meissel's Process for the Volumetric Estimation of Phosphoric acid in Superphosphates.** By CHARLES GLASER (*Chem. Zeit.*, 1894, **18**, 1533—1534).—The author has slightly modified this process. Two grams of the sample is repeatedly lixiviated with water, and the liquid is made up to 250 c.c., and filtered. Fifty c.c. is then titrated with N/10 soda, using methyl-orange as indicator until the red colour has entirely disappeared; this, however, requires some practice. Each c.c. of soda = 0.0071 gram of free  $P_2O_5$ . After adding a solution of calcium chloride and a little phenolphthaleïn, the titration is continued until the liquid shows alkalinity; that this soon disappears makes no difference. Each c.c. of soda represents 0.0035 gram of  $P_2O_5$  present as mono-calcium phosphate.

L. DE K.

**Estimation of Sulphur and of Chlorine with Sodium Peroxide.** By ALBERT EDINGER (*Ber.*, 1895, **28**, 427—428).—The determination of sulphur in organic compounds is readily effected by means of sodium peroxide; chlorine in presence of sulphur can also be estimated in this way. A convenient method of analysing sulphonic acids and mercaptans is to evaporate a 4 per cent. solution of sodium peroxide with the substance in a platinum dish, and, after gently igniting the residue, extracting it with a concentrated solution of sodium peroxide. Chlorine in tetrachloroquinone may be determined in a similar manner, whilst both the platinum and chlorine in platino-chlorides of quinoline derivatives can be estimated in one operation.

M. O. F.

**Estimation of Sulphur in Pig-Iron and Steel.** By JOS. SPÜLLER and S. KALMAN (*Chem. Zeit.*, 1894, **18**, 2039—2040).—The sample is dissolved in hydrochloric acid (sp. gr. 1.17), and the gases are passed through a 3 per cent. solution of sodium peroxide. The last traces of

hydrogen sulphide are removed by means of a current of air which has been purified and also deprived of most of its oxygen by passing it through solutions of mercuric chloride and alkaline pyrogallol.

The alkaline solution is first boiled, and traces of undecomposed peroxide are decomposed by adding potassium permanganate. Any excess of the latter is decomposed by adding hydrochloric acid and a trace of oxalic acid, and the liquid is then precipitated with barium chloride.

L. DE K.

**New Process for Estimating Potassium.** By H. SCHWEITZER and E. LUNGWITZ (*Chem. Zeit.*, 1894, 18, 1320—1322).—The authors use the following process when analysing potash mixtures containing much sulphate; for instance, kainite, superphosphates, &c. The substance is dissolved in water and mixed with an excess of solution of barium oxalate in hydrochloric acid to precipitate the sulphuric acid. After boiling, any iron is oxidised by means of a few drops of hydrogen peroxide, and the iron, calcium, and aluminium, together with any phosphoric acid, and also the excess of barium oxalate, is precipitated by ammonia. The filtrate is evaporated, the residue calcined, and the potassium estimated by means of platinic chloride, as usual.

L. DE K.

**Estimation of Calcium and Magnesium Carbonates in Soils, Ashes, &c.** By ALBERT TRUBERT (*Compt. rend.*, 1894, 119, 1009—1010).—A given weight,  $p$ , of the dried substance is treated with dilute hydrochloric acid, and the volume of carbonic anhydride liberated is measured, preferably by conducting the operation in a large flask and collecting the air displaced. The reduced volume,  $V$ , of gas, divided by 11.12377, gives the number of c.c. of normal hydrochloric acid necessary for the exact decomposition of the carbonates. The same weight,  $p$ , of the dried substance is treated with this volume of normal acid, and when decomposition is complete, the residue is washed, dried, and weighed. The difference between  $p$  and the weight of the residue,  $p'$ , is the sum of the weights of the two carbonates,  $p_1$ . Then if  $x$  is the volume of carbonic anhydride liberated from the calcium carbonate, and  $y$  the volume from the magnesium carbonate,  $V = x + y$ . The weight of calcium carbonate in milligrams is  $4.4948 x$ , and of the magnesium carbonate,  $3.7756 y$ . It follows that  $p_1 = 4.4948 x + 3.7756 y$ , and hence  $x = p_1 - 3.7756 V / 0.7192$ , and the weight  $c$  of the calcium carbonate is  $c = 6.2497 p_1 - 23.5963 V$ , and the weight  $m$  of the magnesium carbonate is  $m = 23.5963 V - 5.2497 p_1$ .

Another method is to determine (1) the weight of the two carbonates,  $W$ , present in, and (2) the volume of carbonic anhydride,  $V$ , liberated from, 1 gram of the substance, and (3) the volume,  $V_1$ , of carbonic anhydride liberated under similar conditions from the same weight,  $W$ , of pure calcium carbonate. The volume  $V_2$  liberated from the same weight of magnesium carbonate is then readily calculated;  $V_2 = 50/42 V_1$ . Then  $V_2 - V_1 = v$ , which corresponds to a weight,  $W$ , of magnesium carbonate, whilst  $V - V_1 = V'$ , which corresponds to the weight  $p$  of magnesium carbonate actually present.

The value of  $p$  is given by the expression  $p = Wv'/v$ . The calcium carbonate is obtained by difference.  
C. H. B.

**Separation of Copper from Cadmium, Zinc, and Nickel.** By P. N. RAIKOW (*Chem. Zeit.*, 1894, 18, 1739).—The author (compare this vol., ii, 242) adds to the mixture an acid solution of hydrazine hydrochloride or sulphate, and then, cautiously, a solution of potassium iodide until precipitation ceases. Copper is completely precipitated, whilst cadmium, zinc, and nickel are not affected. The precipitate may then be decomposed by boiling with dilute nitric acid, and the copper precipitated by aqueous potash.  
L. DE K.

**Estimation of Iron and Aluminium in Phosphates.** By W. HESS (*Zeit. angew. Chem.*, 1894, 679—683; 701—708).—The author states that the iron-aluminium precipitates obtained in the Glaser-Jones's alcohol process or the acetate method rarely have a constant composition. It is therefore necessary to first weigh the mixed phosphates, and then to estimate the phosphoric acid either by the molybdate or the citrate method. Glaser's statement that the iron-aluminium precipitate is occasionally free from calcium proved erroneous, but it can be got absolutely free by repeatedly redissolving in hydrochloric acid and reprecipitating by ammonium acetate with addition of some ammonium phosphate.

Operating in this manner, the acetate process is better and more convenient than the alcohol method.  
L. DE K.

**Estimation of Iron and Aluminium in Phosphates.** By FERDINAND JEAN (*J. Pharm.*, 1895, [6], 1, 99—101).—The author recommends the following method as giving very good and trustworthy results. Four c.c. of strong sulphuric acid is heated in a porcelain basin until it begins to fume; about 1 gram of the finely powdered phosphate is added, and the whole stirred. About half a gram of a mixture of equal proportions of nitrate and chloride of potassium is gradually added to oxidise the iron, then 10 c.c. of water, and the whole is boiled for a few moments. To the cooled liquid, 10 c.c. of alcohol is added, the solution filtered off from the precipitated calcium sulphate, &c., and the latter washed with dilute alcohol. The filtrate is heated on a sand bath until the alcohol is driven off, allowed to cool, 20 c.c. of the ordinary citro-magnesia solution added, and the whole made up to 100 c.c. and left for 12 hours, when all the phosphoric acid is precipitated. Twenty-five or fifty c.c. of the clear supernatant liquid is carefully removed with a pipette, introduced into a flask, evaporated to about 10 c.c., and 5 c.c. of fuming nitric acid added, and boiled for 15 minutes, then 5—6 c.c. of strong sulphuric acid added, and the whole reboiled until it becomes of a coffee colour, when a small quantity of the mixture of nitrate and chloride is added, and the heating continued until the solution becomes colourless. In this way, the citric acid is completely destroyed, and the solution has only to be diluted, and the iron and aluminium precipitated with ammonia in the usual way. The whole operation may be completed in half an hour. The magnesium phos-

phate precipitate in the graduated vessel is collected and weighed as usual as pyrophosphate. L. T. T.

**Qualitative Separation of Nickel and Cobalt.** By A. VILLIERS (*Compt. rend.*, 1895, **120**, 46—47).—The solubility of nickel sulphide in sodium hydrosulphide, when precipitated by hydrogen sulphide from a solution containing sodium tartrate and sodium hydroxide, and the very dark colour of the solution (this vol., ii, 228), can be utilised for the qualitative separation of nickel from cobalt, but cannot be applied in quantitative analysis. The reaction is very sensitive, and indicates the presence of nickel in many so-called pure cobalt salts.

Ammonium salts, if present, must be removed. In the ordinary course of qualitative analysis, the precipitate produced by ammonium sulphide is treated with dilute hydrochloric acid, and the black residue is dissolved in aqua regia, and tested in the manner indicated after removal of the excess of acid. In very dilute solutions of cobalt, this metal may remain in solution unless a considerable excess of sodium hydroxide has been added (*loc. cit.*).

Nickel may be detected more easily, but with less certainty, by means of its solubility in yellow ammonium sulphide, an excess of this reagent being added to the solution containing ammonium chloride and ammonia, but cobalt will also dissolve if the quantity of sulphur in the ammonium sulphide is considerable. C. H. B.

*Note by Abstractor.*—The dark colour of the ammonium sulphide filtrate is already very commonly used as a qualitative reaction for nickel.

**Analysis of Sour Milk.** By MATS WEIBULL (*Chem. Zeit.*, 1894, **18**, 1567—1568).—The author recommends his ammonia process (this vol., ii, 145) for the purpose of collecting daily samples of milk in the same stoppered bottle and then analysing the mixture at a convenient time. L. DE K.

**Oils.** By G. DE NEGRI and GUIDO FABRIS (*Zeit. anal. Chem.*, 1894, **33**, 547—572; from *Publicazione del Laboratorio Chimico Centrale delle Gabelle, Rom.*, 1891 and 1893).—The authors have had under examination 213 specimens of olive oil from various sources, whereof 160 were extracted by themselves from olives of different varieties, partly by pressure, partly by means of solvents, and upwards of 150 specimens of seed oils (also of their own extraction) of the following kinds :—Earth-nut oil, rape-seed oil, jambo oil, oil of black and white mustard, cress oil, radish oil, camelina oil, oil of Dame's violet, almond oil, apricot oil, peach oil, plum-tree oil, cherry-tree oil, cherry-laurel oil, hazelnut oil, beechnut oil, Tormentilla oil, oil of sesamé, cotton-seed oil, cotton-oil margarin, Brazil-nut oil, sunflower oil, Madia oil, pine oil, poppy oil, pistachio-nut oil, maize oil, grape-seed oil, walnut oil, hemp-seed oil, linseed oil, curcas oil, soy oil, coffee oil, oil of laurel, cacao butter, cocoanut oil, mafura fat, and the oils of the Mahwa-Bassia class.

For each kind of oil they give the extremes of specific gravity at  $15^{\circ}$ , the freezing point, melting point of the fatty acids, iodine number, saponification number, and rise of temperature on mixing with sulphuric acid, as also the colour reactions with Heydenreich's, Hauchecorne's, Brullé's, Becchi's, Milliau's, Baudouin's, and Schneider's tests, besides special tests in particular cases, and much information as to methods of detecting those oils which are used for adulterating others. For olive oil, they find the specific gravity to vary between 0.916 and 0.918; the melting point of the fatty acids from expressed oils lies between  $24^{\circ}$  and  $27^{\circ}$ , that of the acids from oils extracted by solvents, which contain more stearin, between  $25^{\circ}$  and  $29^{\circ}$ . The iodine number was in the case of olive oil determined by the use of only a small excess of Hübl's reagent; for the seed oils, a larger excess was used. It was found to be influenced considerably by the variety of the olive and mode of extracting the oil, but very little by the degree of ripeness of the fruit or locality of growth. The limits may be taken as 79.5 to 88, although certain raw unrefined oils gave a number as low as 74.4. The saponification number varied from 185 to 196, but as a rule departed little from 190. The rise of temperature with sulphuric acid, determined with Jean's apparatus, ranged from 32 to 37.

Heydenreich's test consists in letting fall 5 drops of the oil on the surface of pure concentrated sulphuric acid in a porcelain basin, and observing the colours developed during the first three minutes. In Hauchecorne's test, 6 grams of the oil is shaken with 2 grams of nitric acid (of 46.3 per cent.) free from nitrous acid, and the colours are observed after two minutes in the cold, and 20 minutes in boiling water. For Brullé's test, 10 c.c. of the oil with 0.1 gram of egg albumin and 2 c.c. of nitric acid of 1.357 sp. gr. is heated to incipient ebullition. For Becchi's and Milliau's tests see Abstr., 1885, 301, and 1888, 633. Schneider's test consists in saponifying the oil by alcoholic potash and decomposing the soap with dilute nitric acid in presence of silver nitrate, observing the colour at the contact surface of the fatty acids with the aqueous layer. Baudouin's test is given in Benedikt's *Analyse der Fette*, 2nd Ed., 345. With the first four of these tests, olive oil gives, as a rule, only a deep yellow or greenish colour, whilst the seed oils, with the first three reagents, generally give orange-yellow to reddish-brown colours. Unrefined olive oils, which have been extracted by solvents, behave, however, almost exactly like seed oils, and especially give the characteristic Becchi reaction for cotton-seed oil. On the whole, the authors conclude that no single test or determination of constant can be accepted as evidence of the purity of a sample of olive oil, a general view of the reactions and constants being the only means of forming a judgment as to purity.

For the results obtained with the seed oils, the original must be consulted.

M. J. S.

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## General and Physical Chemistry.

**Measurement of the Intensity of Light by the Chemical Changes produced in a Mixture of Ferric Chloride and Oxalic acid.** By GEORGES LEMOINE (*Compt. rend.*, 1895, **120**, 441—444).—The decomposition of a mixture of ferric chloride and oxalic acid in solution (Abstr., 1891, 965) can be used to determine the intensity of light. Although the decomposition is exothermic, the temperature never rises sufficiently high to cause decomposition by heat alone (Abstr., 1893, ii, 405), and the change ceases as soon as the light is cut off. In order to eliminate the effect of physical absorption, the results with layers of liquid of measurable thickness are calculated to a layer infinitely thin, and the intensity is inversely as the time required to produce decomposition in such a layer. Formulæ for this calculation are given. Results are quoted showing that the intensity as measured by the fraction of total decomposition produced in one minute in an infinitely thin layer was 0·16 on a March day, 0·20 on an April day, 0·31 on a May day, 0·24 to 0·29 on September days, and 0·01 on December days.

The same method was applied to the measurement of the intensity of various coloured lights transmitted through coloured media; in summer, the ratio of the intensity of sunlight transmitted through potassium chromate solution was 0·001—0·007, and that transmitted through blue glass or ammoniacal copper solution was 0·40—0·50. C. H. B.

*Note.*—The use of a mixed solution of ferric chloride and oxalic acid for actinometric purposes is very old, and many actinometers based on its use have been constructed (see Eder, *Handb. f. Photographie*, Part I). C. H. B.

**Atomic Refraction of Selenium.** By I. ZOPPELLARI (*Gazzetta*, 1894, **24**, ii, 396—407).—The author has determined the refraction

Substance.	Temp.	$P \frac{\mu_D - 1}{d}$	$P \frac{\mu_D^2 - 1}{d(\mu_D^2 + 2)}$	Atomic refractions for	
				$\mu$ .	$\mu^2$ .
SeEt <sub>2</sub> .....	27·5°	53·10	31·45	19·56	10·94
Se <sub>2</sub> Et <sub>2</sub> .....	21 6	76·79	44·15	21·57	11·82
SeC <sub>6</sub> H <sub>5</sub> .....	26·1	64·63	38·01	19·33	11·18
H <sub>2</sub> SeO <sub>4</sub> .....	24·0	29·79	17·41	16·25	9·22
„.....	25·1	29·39	17·19	15·85	9·00
H <sub>2</sub> SeO <sub>3</sub> .....	25·2	26·84	15·78	15·95	9·12
„.....	26·1	26·98	15·85	16 09	9·19
KSeCN.....	25·0	42·31	25·23	25·79	15·50
„.....	22·1	41·83	24·77	25·30	15·04



constants of a number of selenium compounds for the rays  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and D; the results for the D line are summarised in the table on p. 249.

Ethylic selenide, ethylic biselenide, and selenoxene were examined in the pure liquid state; the two determinations quoted for selenic acid were made in 41.8 and 27.3 per cent. aqueous solutions, and those for selenious acid in 30.6 and 23 per cent. solutions. Potassium selenocyanate was examined in 32.8 and 43.5 per cent. aqueous solutions. The values for selenoxen are calculated on the supposition that this substance has the constitution  $\begin{array}{c} \text{CH:CMe} \\ | \\ \text{CH:CMe} \end{array} > \text{Se}.$

The author concludes that selenium in combination behaves very similarly to sulphur in respect to its refraction constants; the diversity in behaviour of selenium in its various compounds is, however, much less strongly marked than is that of sulphur. It is to be expected that tellurium would behave even more uniformly than selenium; experiments in this direction are now in progress.

W. J. P.

**Spectrochemistry of Nitrogen.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1895, **16**, 497—511 and 512—524; compare this vol., ii, 194).—The author examines the previously determined refraction constants of the various groups of nitrogen compounds; the first paper deals with the amines, and the atomic refraction and dispersion of the nitrogen are calculated in the usual manner. For the primary amines (nine examined), including ethylenediamine and its hydrate, the mean values for the atomic refraction and dispersion are respectively 2.311 and 0.074, the separate numbers being in close concordance (2.45—2.16 and 0.06—0.08). The agreement of the values for the nitrogen in the ethylenediamine hydrate with the remainder indicates, the author considers, that this is a molecular compound  $\text{C}_2\text{H}_4(\text{NH}_2)_2 + \text{OH}_2$ . This mean value is practically identical with the values in ammonia and hydroxylamine. Benzylamine and *ac*-tetrahydro- $\beta$ -naphthylamine give the same numbers, but in those compounds where the nitrogen is directly united to the aromatic ring (eight examined) higher values obtain,  $r_a = 3.016$ ,  $r_\gamma - r_a = 0.624$ . The secondary amines (10) both in the fatty series and the piperidines give the mean values,  $r_a = 2.604$  and  $r_\gamma - r_a = 0.135$ , but where the nitrogen is combined with a benzene group, higher values obtain, namely, 3.408 and 0.815. In the case of tertiary amines (seven), the constants become 2.924 and 0.191, the individual numbers agreeing satisfactorily with the mean. In the aromatic tertiary amines (five), the numbers increase to 4.105 and 1.105. The atomic constants for carbon and hydrogen are also obtained by comparing compounds of the same class differing only by a number of carbon or of hydrogen atoms. The results give 2.347 and 0.07 for carbon (previous values 2.365 and 0.039) and 1.071 and 0.023 for hydrogen (previous values 1.103 and 0.036). In the dichloramines, as would be expected, the values for the nitrogen rise, 3.53 and 0.25.

The second paper deals with constants in the cyanides and the oximes. In the fatty cyanides and dicyanides (nine), the mean atomic

values for the nitrogen are found to be 3.176 and 0.084. Cyanogen, however, gives the values 3.77 and 0.25, and the aromatic cyanides 3.825 and 0.450. It is noticeable that in all these compounds the atomic refraction for the sodium light is less than that for the red  $\alpha$  line. Hydrogen cyanide gives a value (for sodium light) closely agreeing with aliphatic cyanides, and hence its constitution is most probably  $\text{H}\cdot\text{C}\cdot\text{N}$ . The oximes of the aliphatic series give the mean values 3.921 and 0.251, numbers which are greater than those of the triply linked nitrogen. As in the amines and other series, the numbers are increased by the substitution of an aromatic group for a fatty group, the aromatic oximes yielding numbers varying from 4.66 to 5.86 for  $r_a$  and 0.35 to 1.26 for  $r_y - r_a$ . These numbers may be tabulated thus

	$r_a$ .	$r_y - r_a$ .
$\text{H}_2\text{N}-\text{C}-$ .....	2.31	0.07
$\text{HN}(-\text{C}-)_2$ .....	2.60	0.14
$\text{N}(-\text{C}-)_3$ .....	2.92	0.19
$\text{H}_2\text{N}(-\text{Bz})$ .....	3.02	0.62
$\text{HN}(-\text{C}-)$ <sup>Bz</sup> .....	3.41	0.82
$\text{N}(-\text{C}-)_2$ <sup>Bz</sup> .....	4.11	1.11
$\text{N}(-\text{C}-)$ <sup>Bz</sup> <sub>2</sub> .....	4.52	—
$\text{O}=\text{N}=\text{C}$ .....	3.92	0.25
$\text{N}\equiv\text{C}$ .....	3.18	0.08

L. M. J.

**Optical Rotation of Ethereal Salts of Malic acid.** By RICHARD ANSCHÜTZ and HANS REITTER (*Zeit. physikal. Chem.*, 1895, **16**, 493—496).—The authors have determined, at a temperature of 20°, the rotatory power of some ethereal salts of lævo-malic and acetylmalic acids, employing for the purpose a Wild's polaristrobometer. The following results were obtained.

Compound.	$d\ 20^\circ/4^\circ$ .	$\alpha^\circ$ .	$M_{[D]}$ .
Methylic malate .....	1.2334	— 8.449	—11.150
Ethylic malate .....	1.1280	—12.007	—20.226
<i>n</i> -Propylic malate .....	1.0736	—12.455	—25.290
<i>n</i> -Butylic malate .....	1.0382	—11.132	—26.376
Methylic acetylmalate .....	1.1983	—27.398	—46.64
Ethylic acetylmalate .....	1.1169	—25.244	—52.43
<i>n</i> -Propylic acetylmalate .....	1.0729	—24.318	—58.96
<i>n</i> -Butylic acetylmalate .....	1.0430	—20.782	—57.38

L. M. J.

**Gas Batteries. A Correction.** By FRED. J. SMALE (*Zeit. physikal. Chem.*, 1895, **16**, 562—564).—The author makes a correction to be applied to a part of the theoretical portion of his paper on gas batteries (*Abstr.*, 1894, ii, 436), by which it appears that although for a HO-chain the electromotive force is practically independent of

nate is decolorised on heating. Hydrogen cyanide does not give rise to an additive compound. When heated at  $120^{\circ}$ , ethylic acetoacetate-semicarbazide is converted into 3-methylpyrazolone, which is also formed on boiling the aqueous solution.

3-Methylpyrazolone-1-carbonamide,  $\begin{array}{c} \text{N} \text{---} \text{CMe} \\ \text{N}(\text{CONH}_2) \cdot \text{CO} \end{array} > \text{CH}_2$ , is produced when the foregoing compound remains in contact with ammonia for two days; the residue obtained on evaporating the liquid in a vacuum, is dissolved in cold methylic alcohol, and precipitated with ether. The substance melts at  $192^{\circ}$ , and is converted into methylpyrazolone when the aqueous solution is warmed. Ferric chloride develops a blue coloration, which becomes brown when heated.

Ethylic 3-methylpyrazolone-1-carbonyl- $\beta$ -amidocrotonate,



is obtained by agitating semicarbazide hydrochloride with excess of ethylic acetoacetate in presence of soda; it forms small prisms, which melt and decompose at  $176^{\circ}$ . Ferric chloride produces an intense blue coloration. The *sodium* salt is colourless. When distilled in a current of steam, the substance is decomposed into ethylic acetoacetate, ammonia, carbonic anhydride, and methylpyrazolone.

Carbonamidohydrazoisobutyronitrile,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CN}$ , is obtained by the action of hydrogen cyanide on acetone-semicarbazide, and crystallises in prisms, which melt at  $144^{\circ}$ . It has powerful reducing properties, and is decomposed into hydrogen cyanide and acetone-semicarbazide when the aqueous solution is heated on the water bath.

Carbonamidoazoisobutyronitrile,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CMe}_2 \cdot \text{CN}$ , is obtained by oxidising the hydrazo-compound with potassium permanganate in presence of sulphuric acid; it forms lemon-yellow plates, which melt at  $78^{\circ}$ . It is decomposed by cold, dilute alkalis, with liberation of nitrogen, carbonic anhydride, ammonia, and isopropyl cyanide.

Carbonamidohydrazoisobutyramide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CONH}_2$ , is formed by the action of fuming hydrochloric acid on the nitrile; it melts and decomposes at  $205\text{--}206^{\circ}$ . When oxidised with potassium permanganate, it yields carbonamidoazoisobutyramide, which separates from hot water in deep yellow crystals, and melts and decomposes at  $151^{\circ}$ .

Carbaminazoimide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_3$ , is obtained by adding sodium nitrite (1 mol.) to the aqueous solution of semicarbazide hydrochloride; it crystallises in large prisms, which melt at  $92\text{--}93^{\circ}$ . The aqueous solution is acid, and yields azoimide when boiled. Mercuric chloride produces a white precipitate. The dry solid is volatile, and explodes when heated. One half the total quantity of nitrogen is liberated by a cold solution of stannous chloride in hydrochloric acid. The colourless, highly explosive, *silver* salt is insoluble in water; it dissolves in ammonia and in dilute nitric acid, whilst concentrated acid decomposes it into silver azoimide, carbonic anhydride, and

with permanganates, the acid appears to be a strong monobasic acid of acidity equal to nitric acid, but unstable and easily decomposed, as evidenced by the rapid fall in its conductivity.

The second portion of the paper contains experiments on the affinity constants of the saturated fatty acids. A table of the anion velocities is first calculated, the values decreasing from 51.4 in the case of formic acid to 26.0 in the case of pelargonic acid, and agreeing well with the general law of Bredig (*Abstr.*, 1894, ii, 227). The affinity constants of the acids considered are contained in the following table.

Acid.	K (= 100 <i>k</i> ).	Acid.	K (= 100 <i>k</i> ).
Formic .....	0.0214	Capric .....	0.00138
Acetic .....	0.00180	Isobutylic .....	0.00145
Propionic .....	0.00134	Diethylacetic .....	0.00189
Butyric .....	0.00152	Heptic .....	0.00131
Isobutyric .....	0.00143	Caprylic .....	(0.00144)
Valeric .....	0.00150	Pelargonic .....	(0.00112)
Isovaleric .....	0.00167		

The affinity constants also determined for series of isomeric derivatives of hippuric acid and the heats of combustion (observed by Stohmann) are also added, the relative order of this constant for the isomerides agreeing with that of the conductivity.

L. M. J.

**Radiation at Low Temperatures.** By RAOUL PICTET (*Zeit. physikal. Chem.*, 1895, 16, 417—449).—In the first experiments recorded, five calorimeters were cooled to a temperature of about  $-165^{\circ}$ , and allowed to regain the ordinary temperature. Of these one was unprotected, and the other four had coverings of cotton-wool of various thicknesses. The curve of heating was thus obtained for each vessel, constructed with time abscissæ, and as ordinates, the rate of flow of heat per unit of superficial area. From  $-165^{\circ}$  to  $-100^{\circ}$  all the curves lie close together and are practically coincident; from  $-100^{\circ}$  to  $-70^{\circ}$  they begin to widen, but the protective influence of the cotton-wool is not yet at all proportionate to its thickness. All show that at these low temperatures the gain of heat is much greater than that corresponding with the Newtonian curve which is obtained by extrapolation from the results above  $0^{\circ}$ . At about  $-80^{\circ}$  the curves bend more or less sharply and resemble in form the Newtonian curve, while in their concluding portion  $-20^{\circ}$  to  $+10^{\circ}$  protective influence of the cotton-wool appears more and more proportional to its thickness. At  $-165^{\circ}$  to  $-70^{\circ}$ , moreover, no difference is noticed if the cotton-wool is replaced by cork, wood, glass, sand, &c. The author next describes some noteworthy anomalies in the crystallisation of chloroform, which in the smaller of two refrigerators crystallised at from  $-68.5^{\circ}$  to  $-69.5^{\circ}$ , but in the larger remained liquid at  $-81^{\circ}$ . The author considers that the ordinary non-conducting materials have for heat at very low temperatures very different diathermancy from that which they possess for

ordinary heat rays, being almost perfectly transparent in the former case, and this conclusion explains the recorded observations. The physiological effects of low temperatures were studied by placing (1) a dog, and (2) the author himself in the refrigerator, the head being kept outside in both cases. The author states that he felt no cold but an indescribable tickling sensation in both the exterior and interior of the body. The pulse rose to 67 and the respiration to 19 per minute, while a most marked sensation of hunger was experienced. After leaving the refrigerator a very sharp "pins and needles" sensation lasted for about a quarter of an hour, and he states that for the first time in six years he was able to enjoy food. He has since repeated the experiments many times with precisely the same effects, the low temperature being, he considers, beneficial as a powerful digestive stimulant.

L. M. J.

**Correction of Thermochemical Measurements.** By ADOLFO BARTOLI and ENRICO STRACCIATI (*Gazzetta*, 1894, 24, ii, 432—437).—The authors have calculated from their measurements of the specific heat of water (Abstr., 1893, ii, 443), a table serving for the correction of calorimetric determinations.

W. J. P.

**Acid Chlorides and Chloraldehydes.** By PAUL RIVALS (*Compt. rend.*, 1895, 120, 560—562).—The acid chlorides were decomposed by dilute aqueous potash, and the heat of decomposition by water was calculated from these results.

*Chloracetic chloride*, which is readily obtained in large quantity by the action of chlorine on acetic chloride in presence of iodine, gave the following results.

Heat of decomposition by water .....	+69.8	Cal.
$C_2H_2ClOCl$ liq. + $H_2$ liq. = $C_2H_2ClO_2H$ sol.		
+ $HCl$ gas.....	develops + 9.4	"
Heat of formation from elements.....	+24.25	"
$C_2H_3OCl$ + $Cl_2$ = $C_2H_2ClOCl$ liq. + $HCl$		
gas .....	develops +27.1	"

*Trichloracetic chloride*—

Heat of decomposition by water .....	+24.8	Cal.
$C_2Cl_3OCl$ liq. + $H_2O$ liq. = $C_2Cl_3O_2H$ sol.		
+ $HCl$ gas .....	develops + 4.5	"
Heat of formation from elements.....	+93.2	"
$C_2H_3OCl$ liq. + $3Cl_2$ = $C_2Cl_3OCl$ liq. +		
$3HCl$ gas .....	develops +31.5 × 3.	

The heats of decomposition by water are not greatly different from those of acetic (+23.3), butyric (+21.7), and valeric (+20.17) chlorides, as determined by Berthelot and Louguinine, or malonic chloride (+22.1 × 2), as recently determined by Berthelot.

The heats of formation of acetic, chloracetic, and trichloracetic chloride increase somewhat regularly, and the heat of formation of dichloracetic chloride will be about 80 Cal. The substitution of one,

two, and four atoms of chlorine for hydrogen in aldehyde, with formation of the acid chlorides, will develop  $+29\cdot6$ ,  $+28\cdot35 \times 2$ , and  $+31\cdot3 \times 4$  Cal. respectively. The corresponding substitutions in acetic acid develop  $+28\cdot2$  Cal. for monochloracetic acid, and  $+30\cdot3 \times 3$  Cal. for trichloracetic acid. The excessive thermal disturbance in the last case corresponds with the fact observed by Louguinine, that the heat of dissolution of trichloracetic acid is positive, whilst that of acetic and chloracetic acids is negative.

C. H. B.

**Barium Nitride.** By MARCELLIN BERTHELOT and CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], 11, 744).—The heat of dissolution of the anhydrous barium nitride is  $-7\cdot8$  Cal. JN. W.

**Calorimetric Behaviour of Saline Solutions; Sodium Acetate.** By E. MONNET (*Compt. rend.*, 1895, 120, 500—501).—Sodium acetate dissolves in water with absorption of heat, and the author has determined the variation in the heat of dissolution in the resulting solution by measuring the heat absorbed by the dissolution of varying weights of the salt in a constant weight of water. If  $S$  is the concentration of the solution, that is, the ratio of the weight of the hydrated salt to the weight of water added to it, and  $Dh$  the heat absorbed in minor calories, the results are as follows.

$S$ .....	0·04	0·08	0·12	0·16	0·20
$Dh$ .....	34·63	34·93	35·07	35·19	35·27

It is obvious that the heat of dissolution increases with the concentration of the solution, and consequently the dilution of a solution causes the liberation of heat. The determinations of the heat of dilution have been carried as far as a concentration of  $28\cdot5$ . At  $15^\circ$ , the curve obtained by taking the concentrations as abscissæ and the heats of dilution as ordinates is almost rectilinear between concentrations 0 and 10, and rises rapidly; there is a distinct curvature between concentrations 5 and  $17\cdot5$ , and above  $17\cdot5$  the curve tends to become asymptotic to a right line parallel with the axis of the abscissæ of which the ordinate would be about 18. C. H. B.

**Dissolution of Solids in Vapours.** By P. VILLARD (*Compt. rend.*, 1895, 120, 182—184).—The results obtained by Pictet (this vol., ii, 201) with an alcoholic solution of alizarin are similar to those previously obtained by the author with iodine and carbonic anhydride (*J. de Phys.*, 1894, [3], 3). If liquid carbonic anhydride is enclosed with a small quantity of iodine in sealed tubes, as the temperature rises the vapour above the liquid is colourless up to the critical point, when the violet tint is diffused throughout the tube. If, however, the iodine is placed at the top of the tube, the vapour above the liquid dissolves part of the iodine, and may acquire a colour deeper than that of the liquid. Until the critical point is reached, there is a neutral zone above the meniscus. At a low temperature, if the tube is agitated, the vapour is much less coloured than the liquid, but the difference disappears at the critical point. The solubility of the iodine in the liquid carbonic anhydride is very slight at  $-40^\circ$ , but

increases rapidly with the temperature. It is not, however, necessary that the vapour be saturated; a distinct coloration is observed at about 20—25° with gaseous carbonic anhydride compressed below its maximum tension.

In view of these facts, it seems unnecessary to assume that the solution of the solid is due to liquid vesicles suspended in the vapour (*loc. cit.*). The absorption spectrum of either the liquid or the vapour shows none of the channelled spaces characteristic of gaseous iodine, and hence it would seem that the iodine is truly in solution in the vapour, even when the latter is not saturated. C. H. B.

**Application of the Schroeder-Le Chatelier Law of Solubility to Solutions of Salts in Organic Liquids.** By C. E. LINEBARGER (*Amer. J. Sci.*, 1895, **49**, 48—53).—Schroeder and Le Chatelier have independently shown that the solubility of a substance may be calculated by means of the relationship

$$\log_e s = \frac{\rho}{2} \frac{T_0 - T}{T_0 T},$$

in which  $s$  is the solubility, defined by the ratio of the number of the molecules of the dissolved substance to the total number of molecules making up the saturated solution,  $\rho$  the molecular latent heat of fusion of the dissolved substance,  $T_0$  the absolute point of fusion of the dissolved substance,  $T$  the temperature at which saturation takes place. The author discusses data on the solubility of inorganic salts in normal organic liquids in the light of this law. The solubilities of mercuric and cupric chlorides in ethereal salts, of mercuric chloride, bromide, and iodide in carbon bisulphide, and of mercuric chloride, cadmium iodide, and silver nitrate in benzene are considered. No trace of the applicability of the law is found in these cases. H. C.

**New Application of the Principle of the Reduction of Solubility to the Determination of Molecular Weights.** By ST. TOLLOCZKO (*Ber.*, 1895, **28**, 804—809).—Nernst (*Abstr.*, 1890, 1369) has shown that the relative decrease in solubility towards some second liquid which a solvent undergoes, owing to the addition of some foreign substance, is as the number of molecules of the dissolved foreign substance to the number of molecules of the solvent. As no simple application of this principle has yet been devised, the author proposes the determination of the decrease in solubility by the volumetric method. The only apparatus required for the purpose is a flask with a long, thin, calibrated neck. The liquids most suitable for general use are water and ether, and a mixture of these is placed in the flask, the solutions being so adjusted that the boundary between them lies in the neck of the flask. The foreign substance, the addition of which alters the solubility of the ether in the water, is now added, and, when equilibrium is again established, the boundary will be found in some new position in the neck of the flask, the displacement being proportional to the decrease in solubility.

If  $L_0$  is the solubility of pure ether in water, and  $L$  the solubility

after the addition of  $g$  grams of foreign substance of molecular weight  $M$ ,

$$\frac{L_0 - L}{g} M = C.$$

$C$  is a constant, and obviously represents the decrease in the solubility of ether in water on the addition of 1 gram-molecule of the foreign substance.  $C$  will vary with the apparatus used, and also with the relative amount of ether used in the experiment, but may be determined once for all for any given apparatus and quantity of ether by making a determination with a substance of known molecular weight, such as naphthalene. Great care must be taken to keep the temperature as constant as possible while carrying out a determination, if possible within  $\frac{1}{10}^{\circ}$ . The author's test experiments gave satisfactory results.

H. C.

**Isomorphous Mixtures.** By FRITZ W. KÜSTER (*Zeit. physikal. Chem.*, 1895, **16**, 525—528).—Ambronn and Le Blanc have objected to the term isomorphous "mischungen," inasmuch as by this word is usually understood a molecular interpenetration, and considers the term isomorphous "gemenge" more applicable; with this objection the author does not agree.

L. M. J.

**Atomic Weights.** By PAUL E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, **120**, 361—362).—The same considerations that enabled the author to predict with some accuracy the atomic weight of gallium, and to correct that of germanium, lead to the conclusion that there is a family of elements, of which argon seems to be the first known member. The elements in this group will be of a non-metallic character, and will have the atomic weights  $20.0945$ ,  $36.40 \pm 0.08$ ,  $84.01 \pm 0.20$ , and  $132.71 \pm 0.15$ , if  $O = 16$ . Theoretically, they should be octovalent, but they will have little tendency to enter into combination at all. The elements with atomic weights  $20.0945$  and  $36.40$  should be relatively abundant, but the other two, and especially the last, will be rare. The element  $36.40$  should be more volatile than sulphur, and the element  $20.0945$  more volatile than oxygen, whilst  $84.01$  and  $132.71$  should be more volatile than selenium and tellurium respectively.

The author agrees with Ramsay and Rayleigh in placing argon in Mendeléeff's eighth group, to which all the four elements referred to above probably belong.

C. H. B.

**Velocity of the Reaction between Ferric and Stannous Chlorides.** By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1895, **16**, 546—561).—The equation representing the action between ferric and stannous chlorides is of the third order, not of the second order, as stated by Kahlenberg (*Abstr.*, 1894, ii, 346), *i.e.*, is  $2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4$ ; hence the velocity should be given by the equation  $dx/dt = c_3(A-x)(B-x)^2$ . The experimental proof of this is obtained in the far greater constancy of the constant derived from this equation than of that calculated on the assumption that the action is of the



second order, and also by the fact that excess of ferric chloride caused a much greater alteration of the velocity than an equivalent excess of stannous chloride. In neutral solutions, also, Kahlenberg's own numbers give a more constant value for the third order constant than for that from the second order reaction. If acid be added, the values for  $c_3$  do not show such satisfactory constancy, and the action apparently approximates to the second order, but the author is unable to satisfactorily determine the exact nature of the rôle played by the acid.

L. M. J.

**Velocity of Etherification of Methylic Alcohol.** By EMIL PETERSEN (*Zeit. physikal. Chem.*, 1895, **16**, 385—410).—The velocity of etherification in alcoholic solutions was determined by two methods—(1) a direct method; (2) an indirect method, in which a small quantity of methylic chloride is added to the reacting liquids. In the first case, the velocity is obtained by the equation  $dx/dt = k(P-x)(Q-x) - k'x^2$ , where  $P$  and  $Q$  are the initial concentrations. If the ratio  $k'/k = \frac{1}{4}$ , as in very many cases, this expression is reducible after integration to the form  $K = \frac{1}{t} \log \frac{P-x/a}{P-x/b}$ .

When the indirect method is employed, the expression becomes  $K = \frac{1}{Qt} \log \frac{P}{P-x}$ , where  $Q$  is the initial concentration of the methylic chloride, and  $P$  that of the acid. The experiments were performed at the temperatures of 100° and 66°, jackets of steam or methylic alcohol vapour being employed. Formic, acetic, glycollic, oxalic, malonic, succinic, malic, tartaric, racemic, and citric acids were examined by the direct method, but the results were not in all cases trustworthy. The results of the experiments performed by the indirect method are given in the accompanying table of the values of  $K$ . It is noticeable that the ratios of the velocity at 100° to that at 66° vary only between about 2.5 and 3.0, and the author hence concludes that the alteration is due chiefly to change in the molecular properties of the methylic alcohol.

Acid.	T = 100°.		T = 66°.	
	V = 5.	V = 10.	V = 5.	V = 10.
Acetic .....	23.3	26.5	9.0	8.9
Propionic .....	18.7	21.6	6.7	7.7
Butyric .....	11.7	11.6	4.5	4.2
Isobutyric .....	7.7	9.6	3.1	3.4
Valeric .....	3.6	4.2	1.2	1.4
Benzoic .....	0.30	0.28	—	—
Paratoluic .....	0.25	0.25	—	—
Orthotoluic .....	0.095	0.075	—	—
Salicylic .....	0.016	0.015	—	—

L. M. J.

**Relative Affinities of Organic Bases in Alcoholic Solution.**

By ZDENKO H. SKRAUP (*Monatsh.*, 1894, **15**, 775—786).—In order to check the results obtained by observation of the specific conductivity in aqueous solution, the author has taken advantage of the known fact that optically active bases in alcoholic solution frequently show a different specific rotatory power from that of their salts. By ascertaining the change in specific rotatory power which occurs when an optically inactive base is added to a salt, say the hydriodide of an optically active base in alcoholic solution, it becomes possible to determine the relative affinities of the bases. Working on such lines, the values 1, 1.4, 3, 5, and 21 were obtained for cinchonidine, trimethylamine, benzylamine, ammonia, and methylamine respectively. These numbers are somewhat different from those obtained by Bredig, who, from their behaviour in aqueous solution, gives the values 0.0074, 0.0025, 0.0023, and 0.050 for trimethylamine, benzylamine, ammonia, and methylamine respectively. G. T. M.

**The Formation of Oximes.**

By UGO PRATI (*Gazzetta*, 1894, **24**, ii, 310—316).—The action between acetone and hydroxylamine hydrochloride,  $\text{CMe}_2 + \text{NH}_2\cdot\text{OH}\cdot\text{HCl} = \text{CMe}_2\cdot\text{NOH} + \text{HCl} + \text{H}_2\text{O}$ , is a reversible one, so that at a certain time after the commencement of action between molecular proportions of these substances a state of equilibrium is attained. If  $K$  be the velocity of the above reaction, and  $K_1$  that of the reverse change, the course of the action should be represented by a differential equation of the form

$$dx/dt = K(A - X) - K_1X^2;$$

on determining the ratio  $K_1/K$  after equilibrium has become established, this equation can be integrated and the values of  $x$  calculated. Experiments made with solutions of various concentrations at  $10^\circ$  show that the above expression closely represents the course of the reaction; equilibrium becomes established when about one-third of the acetone present is converted into the oxime.

If the action proceeds in presence of sufficient alkali to neutralise the whole of the hydrochloric acid liberated, its course should be represented by an equation of the form  $dx/dt = K(A - X)^2$ , which on integration gives the constant  $K = X/At(A - X)$ . Experiments made in presence of baryta show that, owing to secondary actions,  $K$  is not constant, but diminishes continuously as the time increases.

The author further gives the results of a preliminary investigation of the action occurring between hydroxylamine hydrochloride and acetylacetone. W. J. P.

**Theory of Dyeing.**

By GEORG V. GEORGIEVICS (*Monatsh.*, 1894, **15**, 705—717).—The author has more closely examined the process of dyeing silk with indigo-carmin, and finds that the sulphuric acid added to the dye-bath has a twofold function. It liberates the acid dye, and further, when employed in excess, plays the same part as the salt added during the dyeing of cotton with benzidine dyes. In

the case of the process under investigation, the coefficient of distribution,  $\frac{\text{dye taken up by fibre}}{\text{dye remaining in bath}}$ , is not a constant, but gradually decreases with an increasing concentration of the dye-bath. The expression  $\frac{\sqrt{\text{dye remaining in bath}}}{\text{dye taken up by fibre}}$ , on the other hand, is a constant, and it would therefore appear that simple colour molecules are fixed on the silk, although the dye exists in the bath chiefly in the form of complex double molecules. Henry's law, extended by van't Hoff and Nernst, appears to hold perfectly good in dyeing silk a light indigo-carmin. The value of the coefficient of distribution is greatest for the so-called basic dyes, and least for those resembling salts, whilst for acid dyes it occupies an intermediate position. The value  $\frac{x\sqrt{\text{dye remaining in bath}}}{\text{dye taken up by fibre}}$  is a constant for most, if not for all, substantive colours, where  $x$  expresses the measure of the affinity of the dye for the fibre. The influence of the sulphuric acid on the absorption of the acid dyes by the fibre, and the law which holds for the dyeing of silk with indigo-carmin, point clearly against the assumption that a chemical change occurs between the dye and the fibre, and favour the author's opinion that the dyeing of silk with indigo-carmin is a phenomenon analogous to that of solution. G. T. M.

**Apparatus for Reflux or Distillation.** By CARL MANGOLD (*Zeit. angew. Chem.*, 1895, 159).—Into the distillation flask is fitted a tube, A, to which, at a short distance from the top, and opposite to one another, are attached two tubes; one of these is bent upwards and connected with a reflux condenser, whilst the other is attached to a Liebig's condenser, with a cork cut obliquely at the lower end fitted into the top of the tube A; by turning the cork round the vapours may be directed at will into either condenser. L. DE K.

**New Muffle.** By ÉMILE AUBIN (*Bull. Soc. Chim.*, 1894, [3], 11, 596—597).—An additional muffle is placed over, but in the same chamber as, an ordinary muffle, so that it is heated by the waste products from the burners below. It is useful for preliminary incinerations in agricultural analysis, &c., the temperature being such as to readily carbonise the organic matter without risk of fusing the ash. The incineration of the imperfect ash thus obtained is then easily completed at the higher temperature of the lower muffle. The consumption of gas is not greater than in the ordinary form. JN. W.

**Lecture Experiments.** By JAKOB VOLHARD (*Annalen*, 1895, 284, 345—349).—In demonstrating the increase of weight incurred by air acting as a supporter of combustion, it is necessary that the heated charcoal over which the air is led should be in large fragments, otherwise carbon is locally in excess, and the tared balloon becomes filled with the monoxide.

A simple contrivance is described for illustrating by burning

sulphur the increase in weight which oxygen undergoes. A stoppered flask of more than 1 litre capacity is filled with oxygen and weighed. In another stopper exactly fitting this flask are inserted a deflagrating spoon and a mercury manometer. One gram of sulphur is placed in the spoon and ignited, the second stopper being then substituted for the one in the flask, and when the product of combustion has cooled sufficiently to exert only atmospheric pressure, the first stopper is replaced, and the flask is weighed. The sulphurous anhydride may be dissolved in water and added to a strong boiling solution of phosphorous acid in order to demonstrate the presence of sulphur in the gas.

M. O. F.

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## Inorganic Chemistry.

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**Atomic Weight of Oxygen.** By EDWARD W. MORLEY (*Amer. Chem. J.*, 1895, 17, 267—275).—The experiments described in this paper consist of 12 syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. The hydrogen was absorbed in 600 grams of palladium; the oxygen was weighed in two globes. The apparatus in which the water was synthesised and weighed consisted of a thin glass tube 22 cm. by 25 mm. Midway in its length were inserted two tubes, ending within in two platinum jets parallel to the axis of the long tube. The gases passed into the jets through drying tubes filled with phosphoric anhydride, and were ignited by means of sparks passed between platinum wires fused into the tube just above the jets.

These and other experiments will be more fully described in a memoir to be published by the Smithsonian Institution. The results of the present paper may be summarised as follows.

Density of oxygen, latitude 45° . . . . .	1·42895	± 0·000034
„ hydrogen . . . . .	0·08987	± 0·000027
Ratio of densities . . . . .	15·9002	± 0·00061
Vol. composition of water at 0° . . .	2·0027	± 0·00014
Atomic ratio from densities and volumetric ratio . . . . .	15·879	± 0·0011
Atomic ratio, syntheses . . . . .	15·8792	± 0·00032
Mol. weight of water, syntheses . . .	17·8785	± 0·00066

J. J. S.

**Solubility of Sulphur Precipitatum in Carbon Bisulphide.** By EMIL TITTINGER (*Chem. Centr.*, 1894, ii, 267; from *Pharm. Post.*, 27, 297).—The author finds that neither ordinary stick sulphur nor flowers of sulphur is completely soluble in carbon bisulphide. Precipitated sulphur, however, prepared according to the Austrian pharmacopœia, is completely soluble in 5 parts of cold carbon bisulphide. Sulphur precipitated from a calcium hyposulphite solution by hydro-

chloric acid is also soluble if the solution be maintained slightly alkaline, but if the solution is rendered acid, the precipitated sulphur is only partially soluble. E. C. R.

**Hydrate of Nitric acid,  $\text{HNO}_3 \cdot 7\text{H}_2\text{O}$ : Action of Nitric acid on Organic Compounds.** By VICTOR H. VELEY (*Ber.*, 1895, 28, 928—931).—From a consideration of certain physical and chemical properties of aqueous nitric acid, it appears that these undergo decided modification at a stage of dilution at which the composition of the acid (33 per cent.) corresponds with that of a heptahydrate. The electrical conductivity attains a maximum at 30—37 per cent.; the rate of variation of the magnetic rotation changes abruptly at 33 per cent.; and, as the author has previously observed, certain metals (mercury, copper, bismuth) which cannot be made to dissolve in dilute nitric acid when an oxidising agent is present to prevent the formation of nitrous acid, cannot be prevented from doing so when the strength of the acid exceeds 33 per cent. (Silver, however, is an exception to this rule, as silver-foil is not appreciably attacked, even by 37 per cent. acid, in presence of hydrogen peroxide.) The action between nitric oxide and nitric acid, too, is only strictly reversible with concentrations between 30 and 32 per cent.

The author's hypothesis, that the nitration of hydrocarbons is brought about in the first instance by nitrous acid, is confirmed by Cross's observation that jute is converted into a nitroso-derivative by nitric acid containing nitrous acid, but is merely hydrolysed by pure nitric acid; and by those of Behrend and his collaborators, who have shown that dilute nitric acid (1:4) acts on acetone only in the presence of nitrous acid, and that the initial products are isonitroso-acetone and acetylnitric acid. Denninger's observation, that certain hydroxybenzoic acids can be nitrated by nitrous acid alone, may be explained by assuming that nitroso-compounds are formed in the first instance, and are then either decomposed by nitric acid or oxidised by nitric oxide, arising in either case from decomposition of the nitrous acid.

The action of metals on nitric acid is probably analogous, a nitrite being formed in the first instance and decomposed by the nitric acid.

JN. W.

**Products formed by the Slow Oxidation of Phosphorus.** By JACOBUS H. VAN'T HOFF (*Zeit. physikal. Chem.*, 1895, 16, 411—416).—The author draws attention to Ewan's results, proving that the velocity of oxidation of phosphorus is proportional to the square root of the oxygen pressure (this vol., ii, 213), and may hence be due to oxygen atoms or to oxygen ions, and points out further that the activity of the oxygen caused by the slow oxidation of phosphorus may also be due to oxygen ions and not to ozone. A series of experiments were performed to determine the quantity of oxygen rendered active, the results indicating that the amount is a half atom of oxygen per atom of phosphorus, this amount being independent of the nature of the acid of phosphorus produced. Hence, he considers that the activity is not due to ozone, and that this is not formed, at least in the first instance, during the slow oxidation of phosphorus. L. M. J.

**Amorphous Silicon.** By VIGOUROUX (*Compt. rend.*, 1895, 120, 367–370).—The silicon obtained by reduction with magnesium (this vol., ii, 222) is a light maroon-coloured powder of sp. gr. 2·35 at 15°; it readily absorbs gases and water vapour, which can only be expelled at a red heat. It is readily fused and volatilised in the electric furnace, and dissolves in many molten metals.

Amorphous silicon is not affected by heat alone or by hydrogen when heated in it, but fluorine attacks it with incandescence at the ordinary temperature, chlorine at 450°, and bromine at about 500°; whilst iodine has no action, even at high temperatures. When heated in air, the silicon oxidises superficially only, but in oxygen at about 400° it burns vividly, and the temperature is high enough to fuse the silica that is formed. In sulphur vapour, it becomes incandescent at about 600°; nitrogen has no action below 1000°, but at this temperature an amorphous nitride is formed; phosphorus, arsenic, and antimony vapours have no action, and carbon and boron combine with the silicon only in the electric furnace.

Dry gaseous halogen hydracids slowly attack the silicon at a dull red heat; hydrogen sulphide has no action; ammonia is decomposed at a cherry-red heat with formation of silicon nitride and liberation of hydrogen. Water vapour is slowly but continuously decomposed at about the same temperature with formation of silica; sulphurous anhydride has no action, even at 1000°; nitrous and nitric oxides act slowly at 800°, sometimes with incandescence, the silicon combining with both nitrogen and oxygen; phosphoric anhydride and the oxides of arsenic and antimony are reduced below a red heat with incandescence; carbonic anhydride is converted into carbonic oxide between 800° and 1000°, but the latter is not attacked even at 1200°.

No single acid attacks the silicon, and this is true of boiling fuming nitric acid, boiling concentrated sulphuric acid, and even concentrated hydrofluoric acid at 100°.

With two acids or an acid and another substance, however, the silicon is often attacked; for example, at the ordinary temperature by a mixture of nitric and hydrofluoric acid with evolution of nitrogen oxides and silicon fluoride, or slowly at 100° by aqua regia. A mixture of hydrofluoric acid with potassium nitrate or chlorate, or of nitric acid and potassium fluoride, produces a violent action, but with nitric acid and potassium chlorate there is no change.

Silicon reduces silver, zinc, and lead fluorides with incandescence below a red heat, and many metallic oxides are reduced with incandescence at the temperature of the Bunsen burner, and the hydroxides of the potassium and calcium groups are readily decomposed. Potassium hydrogen fluoride acts on the silicon with evolution of hydrogen; lead sulphate and calcium phosphate are reduced by it. Potassium chlorate has no action at the temperature of its decomposition, but if the two substances are intimately mixed and rapidly heated, oxidation takes place; potassium nitrate attacks the silicon only at its temperature of decomposition; alkali carbonates, either fused or in solution, convert it into silica; potassium dichromate, lead chromate, and similar oxidising agents, oxidise it explosively below a red heat.

The amorphous silicon obtained by reduction with magnesium

differs in its properties from the  $\alpha$ -silicon and  $\beta$ -silicon of Berzelius, and resembles rather crystallised silicon. The latter has hitherto been regarded as non-combustible, but, if rapidly heated in oxygen, it takes fire at about  $400^{\circ}$ , and burns with intense brilliancy.

C. H. B.

**Analysis of Silicon.** By VIGOUROUX (*Compt. rend.*, 1895, **120**, 554—557).—Silica is estimated by heating the silicon in dry chlorine at about  $450^{\circ}$ , and afterwards at a higher temperature to ensure decomposition of the silicides. The residue is allowed to cool in hydrogen, and is then weighed. Foreign substances other than silica are left undissolved when the finely-powdered silicon is boiled with a solution of potassium carbonate; the solution contains silica originally present as impurity, and that formed by the action of the alkali on the silicon. Metallic impurities are obtained as sulphates by adding to the silicon a mixture of nitric and hydrofluoric acids free from chlorine, and then concentrated sulphuric acid, drop by drop, until the temperature rises sufficiently high for the commencement of the action on the silicon.

Silicon from quartz and commercial magnesium contained silicon 89.27, silica 3.01, iron and aluminium silicides 7.62, after one treatment with hydrofluoric and nitric acids, and silicon 97.02, silica 0.66, and silicides 2.34, after three treatments.

With purified silica and distilled magnesium the product contained silicon 99.09—99.60, silica 0.63—0.20, other impurities 0.23—0.20, = 100.00.

Silicon, obtained by Berzelius' method, contained from 22.81 to 54.21 per cent., according to the mode of manipulation, the impurities resulting to a large extent from the action of the excess of potassium on the primary products. The process given by Berzelius for the preparation of  $\beta$ -silicon yields a product containing very little silicon. Crystallised silicon, prepared without special precautions, contains about 5 per cent. of impurities, consisting chiefly of metallic silicides, which can be removed by heating in a current of air and afterwards treating with hydrofluoric acid.

C. H. B.

**Action of Water on Coal.** By GEORGES ARTH (*Bull. Soc. Chim.*, 1894, [3], **11**, 619—622).—Powdered coal of various kinds, containing from 1.6 to 8.3 per cent. of oxygen, was subjected to the prolonged action of air, and of stagnant and running water, with the result that neither the composition, nor the yield of coke, nor the calorific power were appreciably affected.

JN. W.

**Haloid Salts of Cæsium.** By NICOLAI N. BÉKÉTOFF (*Chem. Centr.*, 1894, ii, 229; from *Bull. Acad. St. Petersburg*, [4], **2**, 197—199).—The heat of formation of cæsium iodide from cæsium and iodine in solution is 78,400 cal., and the heat of solution of the salt is —8164 cal., which gives as the heat of formation of the solid salt 86,564 cal. A number which is higher than the heat of formation of potassium iodide, namely, 80,130 cal. The molecular volume of cæsium iodide is 57.5. The atomic volume of cæsium is 70.7, that of iodine 25.6, and the sum of the two 96.3. From these data, the volume contraction which takes place during combination is 40.3 per cent., that is more



than in the case of the formation of potassium iodide, which is 22 per cent. This difference, however, is not accounted for by the greater heat of formation of cesium iodide, but, according to the author, is also due to the ratio of the atomic weights of the components; which is another fact in support of the author's views as to the influence of atomic weight on chemical energy. The heat of formation of cesium bromide is 99,800 cal., which is again higher than the number for potassium bromide, namely, 95,300 cal. E. C. R.

**Action of Hydrogen on Cesium Oxide.** By NICOLAI N. BÉKÉTOFF (*Chem. Centr.*, 1894, ii, 229—230; from *Bull. Acad. St. Petersburg*, [4], 2, 247—249).—The author has already shown that the anhydrous oxides of the alkali metals are reduced by hydrogen, whereby one half of the metal is set free and the other half is converted into hydroxide. This action, according to the author's views, is dependent on the ratio of the atomic weight of the metal to the equivalent weight of oxygen, and takes place more easily the higher the atomic weight of the metal. Thus of all the alkali oxides, lithium oxide is the only one which is not reduced by hydrogen. In the case of cesium oxide, on the contrary, the reduction takes place easily at the ordinary temperature. E. C. R.

**Action of Hydrogen on Photographic Dry Plates.** By ERNST COHEN (*Zeit. physikal. Chem.*, 1895, 16, 450—452).—Ordinary silver bromide gelatin plates were soaked in a dilute solution of soda, mixed in some experiments with a solution of platinic chloride. They were then exposed in the dark to the action of a current of hydrogen. After from 15 to 20 hours, the plates were completely blackened by a deposit of silver. The reduction does not occur if the platinum salt is absent, although a small trace is sufficient to cause blackening. The action is hence probably due to the reduction of the platinum salt in the first instance, the reduced metal then reacting with the silver bromide. L. M. J.

**Properties of Calcium Carbide.** By FRANK P. VENABLE and THOMAS CLARKE (*J. Amer. Chem. Soc.*, 1895, 17, 306—310).—The calcium carbide used in the author's experiments was prepared by the Willson Aluminium Company.

**Action of Water.**—One gram of the substance will yield an average of 200 c.c. of gas, which the authors have proved to be practically pure acetylene. On account of the cheapness of the raw materials it ought to make a valuable addition to the illuminating agents.

**Action of Hydrogen.**—This has no action in the cold. On igniting the carbide in a current of hydrogen for five hours, the only action seemed to be the formation of some tarry matter, which partly condensed in the cold part of the tube.

**Action of Air and Oxygen.**—Ignition in a current of air causes the same tarry deposit, but the carbide is otherwise unaffected. Ignition in oxygen causes but a superficial oxidation.

**Action of Hydrogen Chloride.** This has no action in the cold, but at

a red heat the carbide swells up and assumes a dirty white colour, and is to some extent transformed into calcium chloride.

*Action of Chlorine and Bromine.*—Chlorine had no action in the cold, but at a moderate heat a strong action was observed, and the fused mass consisted of calcium chloride. Bromine mixed with air had also no action in the cold, but, on heating, the mass glowed and fused, and was practically changed into bromide. Some gaseous matter, which partially condensed, was also formed. Chlorine water caused a violent evolution of gas which did not ignite spontaneously, but was inflammable, and burnt like acetylene. Bromine water behaved very similarly.

*Action of Acids.*—Scarcely any action was noticeable in the cold, but on heating a gas was given off which burned with a luminous flame. A mixture of the acid with potassium dichromate causes a very vigorous oxidation, but scarcely any inflammable gas. Strong nitric acid attacked the compound, with formation of brownish-red fumes, which also contained an inflammable gas. Glacial acetic acid slowly decomposed the carbide in the cold. Boiling sulphur did not act in the least, neither does carbonic acid.

*Action of Alkalis.*—The carbide, added to some fusing sodium hydroxide contained in a nickel dish, was violently attacked, with formation of acetylene. Sodium dioxide behaved similarly.

L. DE K.

**Transformations of Zinc Sulphide.** By A. VILLIERS (*Compt. rend.*, 1895, 120, 149—151 and 188—190).—The rate of change of zinc sulphide from the protomorphic state (this vol., ii, 224), in which it is amorphous and soluble in solutions of alkali hydrosulphides, to the ordinary state, in which it is crystalline and insoluble, varies considerably with the temperature. When precipitated by hydrogen sulphide from a feebly alkaline solution of zinc oxide, the conversion into the insoluble form is rapid, although not instantaneous, between 70° and 100°, but is almost instantaneous at the latter temperature. A few degrees below 70°, the change does not begin for several minutes; at about 30°, half the sulphide remains soluble after three hours; between 20° and 15°, this stage is only reached after 17 hours; between 15° and 10°, there is no change even after two days; and between 10° and 0°, there is no change after ten days, even in presence of some added crystalline sulphide.

The conversion into the insoluble form takes place more slowly the more dilute the solution, provided that the quantity of alkali is as low as possible; in strongly alkaline solutions the diminution in the degree of alkalinity, consequent on dilution, compensates for the effect of dilution as such. The temperature of transformation rises as the degree of dilution increases, and also rises rapidly when the quantity of alkali present slightly increases. Dissolved salts, and notably ammonium salts and other alkali salts, have the same effect as concentration of the liquid, and greatly accelerate the change. If the amorphous precipitate is subjected to prolonged washing with hydrogen sulphide solution out of contact with air, it completely redissolves, although at a certain stage part of the sulphide has changed to the crystalline form.

C. H. B.

**Crystallisation of Precipitates; Zinc and Manganese Sulphides and Cupric Hydroxide.** By A. VILLIERS (*Compt. rend.*, 1895, **120**, 322—325).—If an alkaline solution containing the soluble amorphous form of zinc sulphide in suspension is frozen and kept at a low temperature for some hours, the sulphide is completely converted into the crystalline insoluble variety, although the temperature of conversion in the liquid is higher than  $100^{\circ}$ . Manganese sulphide in very dilute solution, with a very slight excess of hydrogen sulphide, behaves similarly, and is converted into the green sulphide as observed by Geuther 30 years ago, although the temperature of transformation in the liquid is above  $300^{\circ}$ . It seems probable that this effect is due to internal pressure in the freezing liquid.

Cupric hydroxide, precipitated from dilute solutions of the sulphate at a low temperature, washed at  $0^{\circ}$ , and suspended in water, is completely converted into the blue crystalline compound,  $\text{CuO} \cdot \text{CuH}_2\text{O}_2$ , described by Peligot, if the liquid is frozen and kept at a low temperature for some hours.

C. H. B.

**Basic and Acidic Zinc Sulphide.** By A. VILLIERS (*Compt. rend.*, 1895, **120**, 498—499).—The zinc sulphide precipitated by hydrogen sulphide from a slightly alkaline solution of sodium zinc oxide, or from the same solution after the addition of a slight excess of tartaric acid, is acidic in character, and dissolves in aqueous hydrogen sulphide even in complete absence of alkali. On the other hand, the sulphide precipitated from a solution of the sulphate is basic in character and quite insoluble in hydrogen sulphide. It is usually crystalline, although under certain conditions it can be obtained in an amorphous form. The varying function, sometimes acidic and sometimes basic, of the so-called indifferent oxides and sulphides, is probably due to a difference in molecular condition, more especially in the degree of condensation, analogous to that observed in the case of zinc sulphide.

C. H. B.

**Action of the Spark Discharge on Lead Oxide.** By EMIL WARBURG (*Ann. Phys. Chem.*, 1895, [2], **54**, 727—730).—The author has noticed that under the influence of the spark discharge, lead oxide darkens with formation of the peroxide when placed in a tube filled with oxygen under a pressure of 2 to 5 mm. In a tube of hydrogen at a pressure of 3 to 10 mm., darkening also takes place, probably with formation of metallic lead. In a nitrogen tube, no change occurs. Experiments with other metallic oxides also gave negative results.

H. C.

**Action of Light on Lead Bromide.** By R. S. NORRIS (*Amer. Chem. J.*, 1895, **17**, 189—191).—The darkening of lead bromide by light (Wells, *Amer. J. Sci.*, 1893, **45**, 134) is a much slower process than in the case of the silver salts, and is entirely superficial. A black specimen of the photo-product on being dissolved in water with the addition of a drop or two of nitric acid (dry lead bromide does not entirely dissolve in water), left about 1 per cent. of lead, and analysis showed a loss of 2—4 per cent. of the bromine. In a second experiment, in which a thin layer of the bromide was exposed to

bright sunlight for two weeks, the product was lighter in colour than that which had been exposed for a shorter time and was entirely soluble in water acidified with nitric acid; the author suggests that the lead had oxidised during the long exposure. Carefully purified lead bromide was found to darken rapidly whether in the form of crystals or fused, and whether in an atmosphere of hydrogen or oxygen. The author regards the phenomenon as a simple dissociation.

A. G. B

**Combination of Lead Iodide with Metallic Iodides and Organic Iodides.** By A. MOSNIER (*Compt. rend.*, 1895, 120, 444—446).—The iodide,  $3\text{PbI}_2 \cdot 4\text{NH}_4\text{I} + 6\text{H}_2\text{O}$ , analogous to the lead potassium iodide of Berthelot, but differing from the lead ammonium iodides of Boullay and of Ditte, is obtained in crystals by dissolving lead iodide in a boiling concentrated solution of ammonium iodide. Strictly analogous, but anhydrous, double salts are obtained in a similar manner with tetramethylammonium, tetrethylammonium, and phenylammonium iodides. The iodide,  $\text{PbI}_2 \cdot 2\text{NaI} + 4\text{H}_2\text{O}$ , is obtained in a similar way, and transparent, lemon-yellow crystals of the hydrate,  $\text{PbI}_2 \cdot 2\text{NaI} + 6\text{H}_2\text{O}$ , separate from the mother liquor. Lithium iodide yields the salt  $\text{PbI}_2 \cdot 2\text{LiI} + 4\text{H}_2\text{O}$  under analogous conditions, and iodides of the calcium group yield double salts of the type  $2\text{PbI}_2 \cdot \text{M}''\text{I}_2 + 7\text{H}_2\text{O}$ .

C. H. B.

**Cupric Hydride.** By EDWIN J. BARTLETT and WALTER H. MERRILL (*Amer. Chem. J.*, 1895, 17, 185—189).—When the copper sponge formed by the decomposition of the cuprous hydride produced by the reaction between copper sulphate and hypophosphorous acid is left in contact with the acid, hydrogen continues to be evolved until the hypophosphorous acid is oxidised to phosphorous acid. Other forms of copper failed to produce this effect, except that obtained by reducing finely powdered cupric oxide with hydrogen; this led the authors to suspect that the copper sponge still contained hydrogen and was in reality a hydride. Analysis of the copper sponge indicated the presence of from 2.85 to 3.56 per cent. of hydrogen, corresponding with the formula  $\text{CuH}_2$ ; the copper which had been reduced from oxide by hydrogen contained a similar percentage of hydrogen. It would seem therefore that the oxidation of the hypophosphorous acid only occurs in contact with this cupric hydride, and not in contact with copper (compare the action of palladium, *Abstr.*, 1890, 690); the action is a continuous one and has no effect on the cupric hydride. The authors suppose that the hydride is a sufficiently strong reducing agent to determine the reduction of a water molecule by a hypophosphorous acid molecule.

*Cupric hydride*, when freshly prepared, is a reddish-brown, sponge-like mass, changing to a chocolate coloured powder when freed from acid and boiled for some time. On drying, it retains the latter appearance and does not oxidise hypophosphorous acid until it has been warmed with it, when the reddish colour and the sponginess return. It decomposes syrupy hypophosphorous acid with evolution of non-inflammable hydrogen phosphide. It reduces potassium chlorate to chloride in solution, also the nitrate to nitrite and ammonia,

and the ferricyanide to ferrocyanide. It has been found (Trans., 1878, 33, 308) that the activity of the copper zinc couple is increased by ignition in hydrogen; this the authors ascribe to the formation of cupric hydride.

A. G. B

**Atomic Weight of Yttrium.** By HARRY C. JONES (*Amer. Chem. J.*, 1895, 17, 154—164).—The yttria used in this work was obtained from Rowland and had been purified as described by him (*Chem. News*, 1894, 70, 68; Abstr., 1894, ii, 449); it might contain as a maximum  $\frac{1}{2}$  per cent. of other rare earths. To remove possible traces of calcium, magnesium, manganese, and iron, the author dissolved the yttria in nitric acid, and precipitated it with ammonia; the washed precipitate was then dissolved in nitric acid and precipitated by oxalic acid; the washed oxalate was ignited to obtain the purified base.

Two series of determinations were made; in the one the oxide was converted into sulphate by heating it with sulphuric acid and expelling the excess of acid; all necessary precautions were adopted and these are fully detailed in the paper. The mean value of 10 determinations in this series is 88.94, the maximum being 89.05, and the minimum 88.89 ( $O = 16$ ). In the second series, yttrium sulphate was prepared by dissolving the oxide in sulphuric acid and crystallising, and this was heated in a platinum crucible over the blast-lamp until a constant weight had been obtained. The mean atomic weight from 10 determinations in this series is 88.97, the maximum being 89.03 and the minimum 88.89 ( $O = 16$ ).

The author reviews the determinations which have previously been made and concludes that Cleve's value, which is about 0.15 higher than the author's number, 88.95, is the most correct of these. The true atomic weight is probably still a little lower than the last number.

A. G. B.

**Hydrated Metallic Chlorides.** By HENRI LESCOEUR (*Bull. Soc. Chim.*, 1894, [3], 11, 853—857).—A rejoinder to Sabatier (this vol., ii, 226). The author is guided in the search for hydrates by the vapour-pressures of the salts; Sabatier, by their heats of dissolution.

Manganous chloride crystallises from water with  $4H_2O$ , but with  $2H_2O$  from concentrated hydrochloric acid; the latter hydrate is also obtained by heating the former at  $20^\circ$  or  $100^\circ$ . Magnesium chloride crystallises, with  $4H_2O$  from water at  $100^\circ$ , or from concentrated hydrochloric acid. Ferrous chloride crystallises with  $6H_2O$ , not  $4H_2O$ . The cupric chloride crystallising with  $4H_2O$  is not homogeneous; and the yellow salt obtained by drying this at  $60$ — $80^\circ$  is monhydrated.

JN. W.

**Boron Steel.** By HENRI MOISSAN and GEORGES CHARPY (*Compt. rend.*, 1895, 120, 130—132).—When amorphous boron is fused with reduced iron, it yields a metal containing 10 per cent. of boron, and when this is added to previously fused soft steel, an iron containing boron 0.58, carbon 0.17, manganese 0.30 per cent., with traces of silicon, phosphorus, and sulphur can readily be obtained in large quantity. This alloy can be rolled, is readily worked at a dull red heat, but crumbles under the hammer if too strongly heated. On the whole, it behaves almost like soft steel.

Determinations of the rate of cooling at different temperatures show a critical point indicating a very considerable development of heat at about  $1140^{\circ}$ , the intensity of this development being of the same order as the recalescence of hard steels. The point is recognisable with iron containing various proportions of boron from 10 per cent. downwards. Feebly marked critical points can also be detected at  $1040^{\circ}$ ,  $830^{\circ}$ ,  $730^{\circ}$ , and  $660^{\circ}$ , the three latter apparently corresponding with the points  $a_1$ ,  $a_2$ , and  $a_3$  observed in ordinary soft steel at somewhat higher temperatures. These phenomena establish clearly the displacement of carbon by boron already observed by Moissan (this vol., ii, 220); the point  $670^{\circ}$ , which is so marked with ordinary iron containing carbon, disappears almost entirely and is replaced by the point  $1140^{\circ}$ .

Mechanical tests show that as regards the increase in the breaking strain by tempering, boron-steel behaves like a decidedly harder carbon-steel, although the diminution in the elongation is more marked with the latter. It is very remarkable, however, that tempering has no appreciable effect on the hardness of the boron-steel, and hence the influence of the boron is quite distinct from that of carbon.

C. H. B.

**Iron Boride.** By HENRI MOISSAN (*Compt. rend.*, 1895, **120**, 173—177).—Iron boride is obtained by the action of boron chloride vapour on reduced iron at a dull red heat, or by the direct combination of iron with boron. In the latter case, soft iron is placed in a dish brasqued with boron and heated at  $1100$ — $1200^{\circ}$  in an atmosphere of hydrogen in a tube placed in a coke fire, or the iron is placed in a carbon crucible brasqued with boron and heated in the electrical furnace for a few minutes with a current of 300 ampères and 65 volts, care being taken that the temperature is not too high, otherwise boron carbide will be formed. The product is heated with hydrochloric acid and the residue washed successively with water, alcohol, and ether.

The iron boride  $\text{FeB}$  thus obtained forms brilliant yellowish-gray crystals several millimetres long, sp. gr. at  $18^{\circ} = 7.15$ . It was the only compound obtained although experiments were made at various temperatures.

Iron boride does not alter in dry air or oxygen, but in moist air it becomes covered with an ocreous layer. It is attacked by chlorine at a red heat, with incandescence, and even more readily by bromine, with formation of a double iron boron bromide, but iodine and hydrogen iodide have no action even at  $1100^{\circ}$ . When heated in oxygen, it takes fire and then burns brilliantly without further extraneous heat. In all cases, amorphous iron boride is much more readily attacked than the crystallised compound, and since the action of oxygen on the boride is greatly accelerated by the presence of moisture and carbonic anhydride, the incandescence sometimes observed during the drying of impure amorphous boron may be attributed to the presence of amorphous iron boride.

The boride is attacked by sulphur and phosphorus at high temperatures. Potassium nitrate and potassium chlorate are without action at their melting points, but at higher temperatures attack the boride with incandescence. Fused alkali carbonates and hydroxides decomposed it rapidly and completely. Concentrated or dilute sulphuric

acid has no action in the cold, but the boiling concentrated acid converts it into ferrous sulphate with evolution of sulphurous anhydride. Dilute hydrochloric acid has no action, but the hot concentrated acid attacks the boride slowly. Hydrofluoric acid also acts slowly, whether hot or cold. On the other hand, whilst very dilute nitric acid dissolves the boride only when hot, the concentrated acid attacks it with violence.

G. H. B.

**Combination of Nitric Oxide with Ferric Chloride.** By V. THOMAS (*Compt. rend.*, 1895, **120**, 447—449).—Anhydrous ferric chloride absorbs nitric oxide at the ordinary temperature with formation of a brown compound,  $\text{Fe}_2\text{Cl}_6\text{NO}$ ; at  $60^\circ$ , the product is  $2\text{Fe}_2\text{Cl}_6\text{NO}$ . The same compounds are formed under the same conditions of temperature when nitric oxide is passed into solutions of the ferric salt. At temperatures at which ferric chloride begins to sublime, it is reduced by the nitric oxide.

The ferric compounds are very hygroscopic, and could not be obtained crystallised; in contact with water, they give off nitric oxide, and, when heated in the air, they yield ferric oxide.

When nitric oxide is passed into ether saturated with ferric chloride, until no more gas is absorbed, and the liquid is evaporated over sulphuric acid, the compound  $\text{FeCl}_2\text{NO} + 2\text{H}_2\text{O}$  is obtained in black needles; if crystallisation takes place at  $60^\circ$ , it separates in anhydrous, yellow crystals. This compound dissolves completely in water, without evolution of gas, and yields a pale yellow solution, the colour of which deepens when heated. On addition of alkalis out of contact with air, ferrous oxide is precipitated, but no gas is evolved. The solution gives other reactions of ferrous salts, and the compound seems to be identical with that obtained by Graham by the action of nitrogen oxides on a solution of ferrous chloride.

C. H. B.

### Action of an Electric Current on Fused Metallic Sulphides.

By JULES GARNIER (*Compt. rend.*, 1895, **120**, 184—185).—A crude nickel sulphide was fused in an earthenware tube provided with carbon electrodes, and was subjected to the action of a current of 10 volts and 23 ampères. The conductivity of the mixture remained very regular, but the voltage gradually diminished, although the temperature of the furnace was practically constant. The following table gives the composition of the original substance and of the products round the anode and cathode after passing the current for an hour and then cooling slowly.

	S.	Fe.	Ni.	Cu.
Original substance . . . . .	21.10	33.30	16.30	29.00
Anode product . . . . .	16.60	35.40	5.13	39.90
Cathode product . . . . .	4.70	49.10	19.10	26.13

The sulphur is, to a large extent, eliminated, probably as carbon bisulphide, and the remainder is concentrated at the anode. The quantity of nickel increases from the anode to the cathode, whilst that of copper increases in the reverse direction. The iron, on the whole, tends to accumulate at the cathode.

C. H. B.

**Amidochromates.** By GRÉGOIRE WYROUBOFF (*Bull. Soc. Chim.*, 1894, [3], **11**, 845—853; compare Loewenthal, *Abstr.*, 1894, ii, 383).—The author denies the existence of the amidochromates. Loewenthal's ammonium and potassium amidochromates are identical in crystallographic details with ammonium dichromate. The lithium salt is crystallographically identical with potassium dichromate, an impure lithium compound having probably been used in its preparation. The so-called amidochromates of fixed bases, moreover, do not appreciably lose weight when heated, and, when it is attempted to prepare them by acting on a chlorochromate with ammonia, no ammonium chloride is formed, as should be the case if Loewenthal's statements be correct.

The lithium chlorochromate is crystallographically identical with potassium chlorochromate. JN. W.

**Titanium.** By HENRI MOISSAN (*Compt. rend.*, 1895, **120**, 290—296).—When titanic anhydride is heated in a platinum dish using a current of 100 ampères and 50 volts, it yields a fused, or partially crystalline, deep indigo-blue mass of a lower oxide, which seems to be the monoxide mentioned by Laugier and by Karsten, and which is still under investigation. With a higher temperature, from a current of 300—350 ampères and 70 volts, the product is a fused mass of titanium nitride,  $Ti_2N_2$ . If titanium oxide and carbon are heated in a carbon dish in the tube of the electric furnace with a current of 1200 ampères and 70 volts, a crystalline mass of titanium carbide,  $TiC$ , is obtained, quite free from nitrogen. If a similar mixture with titanium oxide in excess is heated at the same temperature in a crucible, titanium is obtained, containing a variable proportion of carbon. With a current of 2200 ampères and 60 volts, the yield is better, each operation yielding about 200 grams of titanium. Below the titanium in the crucible is a layer of the nitride, and below this a layer of the blue oxide, hence it is clear that the temperature falls rapidly from the top of the crucible to the bottom.

The author regards these results as proof that the temperature of the arc is a continuous function of the current.

The proportion of carbon in the metal varies with the proportions in which the oxide and carbon were mixed. A mixture of titanic anhydride and titanium carbide, heated at the highest temperature already specified, yields a product containing about 4·8 per cent. of carbon, and if this is again heated with excess of the oxide a metal containing only 2 per cent. of carbon, and free from nitrogen and silicon, is obtained.

Titanium, thus prepared, has a brilliant, white fracture, and will scratch rock crystal and steel, but is very friable; sp. gr. = 4·87. It is attacked by chlorine at 325° with incandescence, and by bromine at 360° with incandescence, but by iodine only at a higher temperature, and without incandescence, the product being the solid iodide. In oxygen it burns at 610°; in sulphur vapour, at the softening point of glass, it forms a dark coloured sulphide, which is not affected by cold hydrochloric acid, but is attacked by the boiling concentrated acid; in nitrogen at about 800° the powdered metal is converted into



nitride with development of heat; phosphorus at  $1000^{\circ}$  converts it superficially into a dark coloured phosphide.

Carbon dissolves in fused titanium and forms a definite carbide, any excess separating as graphite; boron and silicon yield a fused or crystalline boride or silicide as hard as the diamond. Titanium dissolves in iron and lead, and it forms alloys with tin and chromium.

Titanium is attacked by concentrated boiling hydrochloric acid with evolution of hydrogen and formation of a violet solution; slowly by nitric acid, but more rapidly by aqua regia; more readily by dilute sulphuric acid in the cold, with liberation of hydrogen and production of a violet solution, also by the hot concentrated acid, with evolution of sulphurous anhydride; very readily with effervescence by a mixture of nitric and hydrofluoric acids. It is also attacked without development of heat by fused potassium nitrate, readily with brilliant incandescence by fused potassium chlorate, and also with incandescence by fused alkali carbonates, alone or mixed with potassium nitrate. Powdered titanium decomposes steam at about  $700^{\circ}$ , but the reaction is not continuous below  $800^{\circ}$ . It reduces silver fluoride at  $320^{\circ}$  with incandescence.

*Titanium carbide*,  $TiC$ , is obtained by the action of an arc from a current of 1000 ampères and 70 volts on a mixture of titanium oxide with excess of carbon, and is a fused mass with a crystalline fracture, or is partially crystallised; sp. gr. 4.25. It is not attacked by hydrochloric acid and only slowly by aqua regia, and it does not decompose steam at  $700^{\circ}$ , but in other respects its reactions are similar to those of titanium, except that it burns much more readily in oxygen.

*Titanium nitride*,  $Ti_2N_3$ , obtained under the conditions already described, is a bronze-yellow mass of sp. gr. 5.18; it scratches rubies and will cut diamonds.

C. H. B.

**Bismuth Sulphide.** By ALFRED DITTE (*Compt. rend.*, 1895, 120, 186—188).—Amorphous precipitated bismuth sulphide dissolves readily in a cold solution of potassium sulphide, in proportion increasing with the quantity of alkali sulphide present, and forms a red solution. If an excess of bismuth sulphide is added and the liquid is heated, a further quantity dissolves, and, when the solution is sufficiently concentrated and is allowed to cool, it deposits very brilliant, transparent, highly refractive, reddish-yellow rhombohedra, of the composition  $Bi_2S_3 \cdot 4K_2S + 4H_2O$ . The crystals effloresce in dry air, and in moist air become covered with a black film of bismuth sulphide. They are immediately decomposed by water with separation of bismuth sulphide, and a similar decomposition takes place on adding a small quantity of water to their mother liquor.

If the amorphous sulphide is placed in a solution of potassium sulphide just sufficiently concentrated to form a small quantity of the double salt, and if the liquid is heated in such a way that the temperature is not uniform, the double sulphide will form in the cooler parts and be decomposed in the hotter parts, and the bismuth sulphide will separate in a crystalline form, not readily attacked by the alkali sulphide. In this way, the whole of the bismuth sulphide may become crystalline, as in the case of silver sulphide (this vol.,

ii, 223). The crystals are small, have the colour and lustre of graphite, soil the fingers, and generally resemble the natural sulphide.

Bismuth sulphide is only slightly soluble in cold saturated solutions of sodium sulphide, and, although on heating the solution, and allowing it to concentrate at the same time, the solubility increases sufficiently to produce a small quantity of double salt, and thus convert the bismuth sulphide into the crystalline form, the liquid does not deposit the double sulphide. C. H. B.

**Gold Sulphide.** By ALFRED DITTE (*Compt. rend.*, 1895, 120, 320—322).—When hydrogen sulphide is passed into a neutral solution of gold chloride, the gold sulphide remains in solution and can pass through a filter, but after some time it separates in a colloidal condition. A small quantity of hydrochloric acid causes immediate precipitation of the sulphide as a black powder.

If the insoluble gold sulphide is mixed with excess of sodium monosulphide, it dissolves to an orange-red solution from which colourless slender needles of the double sulphide,  $\text{Au}_2\text{S}, 2\text{Na}_2\text{S} + 20\text{H}_2\text{O}$ , separate on concentration. This compound is very soluble in water, and acids precipitate gold sulphide from the solution. With very slight excess of the alkali sulphide, slender needles of the sulphide,  $\text{Au}_2\text{S}, \text{Na}_2\text{S} + 10\text{H}_2\text{O}$ , are obtained, whilst the mother liquor contains the disulphide  $\text{Na}_2\text{S}_2$ . It is clear that in contact with sodium sulphide, auric sulphide is reduced to aurous sulphide, which then forms stable double sulphides.

If the gold sulphide is in excess, a small quantity only dissolves and the residue contracts and after some days consists of a dense greenish-yellow crystalline powder of metallic gold. At first aurous sulphide and sodium disulphide are found, but the latter continues to remove sulphur from the gold sulphide until the alkali polysulphide is saturated with sulphur. The double gold sodium sulphide decomposes similarly in contact with the excess of gold sulphide. Alkali polysulphides saturated with sulphur have no action on either gold sulphide or metallic gold.

With potassium sulphide, similar phenomena are observed, but the alkali sulphide and the double sulphide being much more soluble, the isolation of the latter in a pure state is more difficult. The double sulphide,  $\text{Au}_2\text{S}, 4\text{K}_2\text{S}_2 + 12\text{H}_2\text{O}$ , is formed in presence of a slight excess of potassium sulphide and crystallises in needles.

C. H. B.

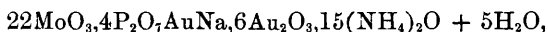
**Complex Inorganic Acids.** By WOLCOTT GIBBS (*Amer. Chem. J.*, 1895, 17, 167—185; compare this vol., ii, 229).—A solution of auro-sodium pyrophosphate,  $\text{AuNaP}_2\text{O}_7$ , yields with ammonia a white precipitate, presumably *sodium auramine pyrophosphate*,



which rapidly becomes yellow and crystalline; when heated above  $170^\circ$  it explodes, indicating that a part of the gold is present in the form of an auramine; when boiled with barium chloride, it yields a yellow crystalline salt, and a silver salt is obtained on the addition of a cold solution of silver nitrate; both these salts were analysed, but the

figures show that in neither case does a simple double decomposition occur between the auramine and the precipitant. Other reactions are described and the author considers the possible constitution of the salt.

An *auropyrophosphomolybdate*,



is obtained as a buff-coloured precipitate when a solution of sodium auropyrophosphate is boiled with one of ammonium molybdate; it does not explode when heated. By boiling with ammonium molybdate, the orange-coloured precipitate which ammonia produces in a solution of sodium auropyrophosphate, a pale, yellowish crystalline salt is formed; this appears to be an *auramine pyrophosphomolybdate*.  $12\text{Au}_2\text{O}_3, 3\text{MoO}_3, 7\text{P}_2\text{O}_5, 24\text{NH}_3 + 21\text{H}_2\text{O}$ ; it explodes when heated.

The author gives the results of some preliminary work on molybdicotungstates, uranosotungstates, silicomolybdates, selenosomolybdates, selenosotungstates, telluroso-molybdates and -tungstates, and cericomolybdates, and describes a new phosphotungstate of the formula  $20\text{WO}_3, \text{P}_2\text{O}_5, \text{Na}_2\text{O}, 2\text{H}_2\text{O} + 19\text{Aq}$ .

A. G. B.

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## Mineralogical Chemistry.

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**Succinite (Amber).** By ALEXANDER TSCHIRCH and E. AWENG (*Arch. Pharm.*, 1894, **232**, 660—688; see this vol., i, 384).

**Cassiterite.** By W. KOHLMANN (*Zeit. Kryst. Min.*, 1895, **24**, 350—365).—Descriptions and measurements of crystals from numerous localities are given under Becke's three types: (1) crystals with equal extension of the vertical and lateral axes, no basal plane and frequently twinned (characteristic of the Erzgebirge); (2) "needle-tin," with an acute pyramid largely developed (Cornwall); (3) basal plane prominent (Pitkäranta). A fourth type is added, in which the pyramid  $s(111)$  predominates. A complete list of crystal forms is given. The variations in colour of the mineral are described, and the colour of a yellow crystal from Perak is attributed (doubtfully) to tungsten; the crystal giving on analysis—

SnO <sub>2</sub> .	WO <sub>3</sub> .	FeO.	Total.
99·90	0·11	0·12	100·13

The modes of occurrence and associated minerals from different localities are described. L. J. S.

**Artificial Spinel and Corundum.** By J. MOROZEWICZ (*Zeit. Kryst. Min.*, 1895, **24**, 281—285).—The analysis of a well crystallised silicate fusion containing plagioclase, nepheline, olivine, magnetite, and 14·45 per cent. of corundum is given under I. The corundum occurs as tabular or pyramidal crystals of a silver-white or yellowish

colour, and consists of 99·5—99·8 per cent. of  $\text{Al}_2\text{O}_3$ ; sp. gr. 4·012. II gives the analysis of a slag containing plagioclase, olivine and 7·21 per cent. of spinel; the latter occurs as simple and twinned octahedra of a yellowish colour; sp. gr. 3·45.

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	CaO.	MgO.	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	Total.
I. Corundum	37·24	{ 29·29 14·45	{ 2·91 —	{ 4·10 —	{ 0·54 —	{ 5·04 —	{ 6·93 —	{ 100·50
II. Spinel . . .	37·79	{ 31·17 4·74	{ 3·17 0·59	{ 5·62 —	{ 7·80 1·94	{ 1·83 —	{ 5·12 —	{ 99·71

It is thus proved that these minerals could separate directly from volcanic magmas, containing an excess of alumina (over 30 per cent.), without the aid of "mineralising agents." L. J. S.

**Pyrogenetic Corundum.** By ALEXANDER E. LAGORIO (*Zeit. Kryst. Min.*, 1895, 24, 285—296).—The corundum of volcanic rocks has previously been assumed to owe its presence by being brought up from below with the magma, or to the action of "mineralising agents." The known occurrences in volcanic and contact rocks are enumerated, and the associated minerals mentioned. This corundum, the typical habit of which is tabular, is confined to rocks containing more than 30 per cent. of alumina; such rocks are however rare, there being no volcanic rocks and even few clay slates. An analysis of an enclosure in andesite from Bockberg, with 47·43 per cent.  $\text{Al}_2\text{O}_3$ , which contains corundum and spinel, is quoted, as well as analyses of some contact rocks containing a high percentage of alumina. Experiments have been made on the solubility of corundum and other infusible minerals rich in alumina, in different silicate fusions (trachyte, andesite, leucite, &c.); the solubility is greater in fusions poor in alumina. The meaning and limitations of the term "mineralising agent" are discussed. L. J. S.

**Sulfoborite.** By HUGO BÜCKING (*Jahrb. f. Min.*, 1895, i, Ref., 253—254; from *Ber. Ak. Berlin*, 1893, 967—972).—Sulfoborite from the salt-beds of Westeregeln, Stassfurt, gave on analysis—

MgO.	$\text{SO}_3$ .	$\text{H}_2\text{O}$ .	$\text{B}_2\text{O}_3$ (diff.).
32·91	21·95	21·50	(23·64)

The formula is given as  $3\text{MgSO}_4 \cdot 2\text{Mg}_3\text{B}_4\text{O}_{10} \cdot 12\text{H}_2\text{O}$ ; sp. gr. 2·38—2·45. The transparent, colourless, or slightly reddish crystals are rhombic with  $a : b : c = 0·6196 : 1 : 0·8100$ . L. J. S.

**Apophyllite from Grängesberg.** By GUSTAF HALLBERG (*Jahrb. f. Min.*, 1895, i, Ref., 268—269; from *Geol. För. Förh. Stockh.*, 1893, 15, 327).—Apophyllite occurs in radial and platey aggregates in stephanite (Schwarzerz) with apatite, calcite, magnetite and pyrites. Analysis gave—

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	CaO.	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	F.	Total.
51·96	0·30	25·0	0·43	4·10	16·96	0·86	99·61

Total, substituting F for O (0.36), = 99.25. In convergent polarised light an optic axial angle of about  $10^\circ$  was observed, with the usual interference colours; optically positive. L. J. S.

**Tourmaline, Gypsum and other Minerals from Bohemia.** By FRIEDRICH KATZER (*Zeit. Kryst. Min.*, 1895, **24**, 428; from *Tsch. Min. Mitth.*, 1891, **12**, 416, 1891).—The modes of occurrence, &c., of several minerals (*e.g.*, mispickel, blende, galena, siderite, quartz, gypsum, wollastonite, andalusite, cordierite, &c.) from various localities are described. Analysis of tourmaline from Kuhrau gave—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	B <sub>2</sub> O <sub>3</sub> .	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.
36.28	31.59	8.76	7.25	6.79	1.41	0.92	2.60
		Na <sub>2</sub> O.	K <sub>2</sub> O.	F.	H <sub>2</sub> O.	Total.	
		1.28	0.41	0.59	2.51	100.39	

Gypsum from Mergeln gave—

CaO.	SO <sub>3</sub> .	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
32.29	45.91	0.41	0.19	20.52	99.32

L. J. S.

**Vulcanite, a New Rock.** By WILLIAM H. HOBBS (*Jahrb. f. Min.*, 1895, i, Ref., 315—316; from *Zeits. deuts. geol. Ges.*, **45**, 578—593).—Vulcanite, an anorthoclase-augite rock forms the crust of blocks ejected from Vulcano in April, 1893; it consists of a glassy base with porphyritic and microlitic felspar and augite, and enclosures of altered dolerite and liparite. The felspar is partly anorthoclase, I gives the analysis of that having a density between 2.56 and 2.60; II the augite; III the bulk analysis of the rock (which is compared with dacite); and IV the ground mass.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> . FeO.		MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
I.	60.01	20.12	2.82		0.23	5.15	3.67	6.43	0.77
II.	47.60	4.66	— 12.73		14.56	18.06	—	1.50	0.50
III.	66.99	17.56	1.41	3.39	0.93	4.25	0.34	3.35	1.53
IV.	67.55	18.04	1.18	3.15	0.74	3.03	0.11	4.39	1.06

L. J. S.

### Physiological Chemistry.

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**Radiation at Low Temperatures and its Employment for Therapeutic Purposes.** By **RAOUL PICTET** (*Zeit. physikal. Chem.*, 1895, 16, 417—449; see this vol., ii, 253).

**The Glycolytic Ferment.** By **RAPHAEL LÉPINE** (*Compt. rend.*, 1895, 120, 139—141).—When the pancreas taken from a dog is crushed under aseptic conditions immediately after its removal from the animal,

and digested for some time at  $38^{\circ}$  with very dilute sulphuric acid (2 : 1000), the solution shows a glycolytic power much higher than that of a fresh pancreas macerated in water containing no acid. It follows that, under the influence of the acid, the glycolytic ferment is produced, probably by hydrolysis, just as, according to Heidenhain, it is developed from trypsin in a pancreas macerated with very dilute sulphuric acid. The author considers, however, that the glycolytic ferment is derived from diastase. He finds that when purified commercial diastase is heated for two or three hours at  $38^{\circ}$  with very dilute sulphuric acid (1 : 1000) the solution loses its saccharifying power, but acquires a well-marked glycolytic power. A similar effect is produced by the action of dilute sulphuric acid on human saliva and on the pancreatic juice itself. It was also observed that during the excitation of the nerve and withdrawal of the pancreatic juice by means of a cannula, the blood of the pancreatic vein had no marked glycolytic power, but acquired this power after some time when there was no flow of pancreatic juice. This balance between the internal and external secretions of the pancreas is under investigation.

C. H. B.

**Digestion of Pseudo-nuclein from Casein.** By JOHN SEBELIEN (*Zeit. physiol. Chem.*, 1895, 20, 443—454).—The pseudo-nuclein from casein (see Hammarsten, *Abstr.*, 1894, i, 310) is of varying composition, and the present research confirms that of Moraczewski (this vol., ii, 54) on the subject. In pancreatic digestions, casein is almost completely digested.

W. D. H.

**Digestibility of Pentosans.** By HUGO WEISKE (*Zeit. physiol. Chem.*, 1895, 20, 489—497).—A review of the previous work on the subject shows that the nutrition value of pentosans is by no means settled. Some researches on the lower animals indicate that these substances form a source of glycogen; in other cases, especially in human beings, they appear to pass unchanged into the urine. The present research, carried out on sheep and rabbits fed on oats and wheat straw, shows that a considerable quantity of the pentosans present in the fodder disappears from the intestines; in the sheep, 62—66 per cent. disappears from the fæces; in the rabbit, the number is 51—55 per cent. This, however, does not necessarily imply that all this had been absorbed, as some might have gone, from the decomposition produced by bacteria, into simple and useless material.

W. D. H.

**Phosphorus and Sugar yielding Constituents of Liver and Suprarenal Bodies.** By PAUL MANASSE (*Zeit. physiol. Chem.*, 1895, 20, 478—488).—It has long been known that the medullary substance of the suprarenal capsules contains a substance which becomes dark brown with salts of chromic acid, unless the capsules have been previously hardened in alcohol. The substance is soluble in alcohol, and shows great similarities to the substance named jecorin, first separated by Drechsel from the liver (*Abstr.*, 1886, 636; 1888, 1313). The resemblance to lecithin noted by Drechsel is



accentuated by the fact that, as the present research shows, it yields choline, glycerophosphoric acid, and fatty acids on decomposition. The carbohydrate obtainable from it, and to which it owes its reducing power, appears by its properties to be most like dextrose.

The substance obtainable from the suprarenals has a general resemblance to jecorin, but differs from it in some of its solubilities, and in the fact that it does not reduce alkaline solutions of copper hydroxide until after prolonged boiling with sulphuric acid; the sugar then formed appears to be dextrose. The following percentage compositions are given.

	Jecorin.		Substance from suprarenals.
	Drechsel.	Baldi.	
C.....	51·32—51·64	46·88—46·89	41·43
H.....	8·11—8·25	7·81—8·09	7·16
N.....	2·86	4·36—4·88	0·3
S.....	1·42—1·47	2·14—2·70	1·8
P.....	2·2—3·7	2·29—2·75	4·44
Na.....	2·72	5·72	—
O.....	30·10	—	—

W. D. H.

### The Silvery Substance in the Skin of *Alburnus Lucidus*.

By ALBRECHT BETHE (*Zeit. physiol. Chem.*, 1895, **20**, 472—477).—The silvery material in the scales of certain fishes is crystalline, and, according to the most trustworthy of previous researches, consists of guanine. The correctness of this hypothesis is confirmed in the present research for the case of *Alburnus lucidus*. W. D. H.

**Oyster Shells.** By G. ADOLPHE CHATIN and ACHILLE MUNTZ (*Compt. rend.*, 1895, **120**, 531—534).—Analysis of the shells of oysters from various sources show that 100 parts of dry shell contain N, 0·05—0·14; SiO<sub>2</sub>, 0·44—1·60; CaO, 48·44—53·70; P<sub>2</sub>O<sub>5</sub>, 0·019—0·089; SO<sub>3</sub>, 0·779—1·004; MgO, 0·340—0·570; Fe, 0·011—0·037; Mn, 0·009—0·017; S (as sulphide), 0·015—0·020; organic matter, 0·90—1·00; F, 0·015—0·020; I, 0·003; Br, 0·005; CO<sub>2</sub>, 43·329—48·122.

The proportion of phosphoric anhydride is considerably higher in the shells of Portuguese oysters than in any others, the usual amount being 0·04—0·05.

The composition of the shells justifies to some extent their use as a manure and in ancient medical practice. C. H. B.

**Acidity of Urine.** By ERNST FREUND and GUSTAV TOEPFER (*Zeit. physiol. Chem.*, 1895, **20**, 455—459).—Polemical, being chiefly concerned in answering the objections of Lieblein (this vol., ii, 55) to the methods previously described by the authors (*Abstr.*, 1894, ii, 260). W. D. H.

**Effect on Butter of Feeding with Sesame and Cotton Cakes.** By V. STEIN (*Bied Centr.* 1895, 24, 93—94).—See this vol., ii, 299).

**Behaviour of Acid-imides in the Animal Organism.** By FR. KOEHLER (*Chem. Centr.*, 1894, ii, 296; from *Inaug. Diss.*, Rostock, 1894).—Succinimide is almost completely destroyed in the animal organism without affecting the health of the animal. The sodium compound of dibenzamide is destroyed and expelled as hippuric acid. Phthalimide is almost completely destroyed without affecting the health of the animal, but the ethereal hydrogen sulphates in the urine are somewhat diminished by this compound. Benzoylcarbamide is without influence on the organism, and is destroyed and expelled as hippuric acid. Ethyl allophanate is without action on the organism and is completely destroyed. On the other hand, biuret, diphenylbiuret, and diphenolbiuret pass through the organism without change. The two latter when administered in large doses cause vomiting. Carbonyldicarbamide is also for the most part recovered unaltered in the urine. In contradistinction to these biurets, the corresponding ring compounds are completely destroyed by the animal organism. Benzylidenbiuret is expelled as hippuric acid; cyanuric acid, which might be expected to appear in the urine, is absent, as this also is completely decomposed. Parabanic acid behaves like cyanuric acid. Alloxan and alloxantin are also in a great measure destroyed, and are expelled in the urine in small quantities as parabanic and oxalic acids. E. C. R.

**The Blood in Cancer.** By WACŁAW v. MORACZEWSKI (*Virchow's Archiv.*, 1895, 139, 385—405).—The blood was examined in a number of cases of cancer and other diseases, the phosphates, chlorides, hæmoglobin, total solids, and nitrogen being determined. From the tables given, there appears very little of a constant change from the normal. A diminution in the amount of phosphates in the blood of cancerous patients seems not to be due so much to the new growth as to the anæmia it produces; the chlorides increase proportionately to the fall in the phosphates; and the proportion of chlorides in the urine to chlorides in the blood falls. A high percentage of nitrogen in the blood distinguishes cancer and also scurvy from simple anæmia. In pulmonary stenosis and asthma, the total solids are high. W. D. H.

**The Contents of Two Lymph Cysts.** By RICHARD v. ZEYNEK (*Zeit. physiol. Chem.*, 20, 1895, 462—471).—Short details of the cases are given, and former literature referred to. The composition of the fluid removed may be stated in tabular form as follows.

	Case I.	Case II.	
		1st tapping.	2nd tapping.
Total proteid. ....	5·069	3·794	4·066 gr. per cent.
Fat (ether extract) ..	8·024	2·312	4·1 „

Total solids .....	14.887	7.463	9.067
Ash.....	0.908	0.764	0.804

The ash from Case I gave—

Soluble in water.							
SO <sub>3</sub> .	Cl.	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
0.07	0.323	0.009	0.049	0.015	0.004	0.021	0.380
Insoluble in water.							
P <sub>2</sub> O <sub>5</sub> .	CaO.	MgO.	CO <sub>2</sub> (diff.).	SO <sub>3</sub> .			
0.021	0.058	0.0005	0.035	0.013			

These fluids were milky; the percentage both of proteïd and fat was high. The proteïds present were chiefly serum-albumin, small quantities of globulin, traces of a phosphorised proteïd, and a variable amount of fibrin, which may be absent. Caseïn and peptone are absent. The fat includes not unimportant quantities of cholesterol, and traces of lecithin. Sugar was absent. Soaps and a small amount of urea were present in both cases. The fluid was found to be very resistant to bacterial action.

W. D. H.

**Levulose and Diabetes.** By KARL BOHLAND (*Chem. Centr.*, 1894, ii, 890—891; from *Therap. Monatsh.*, 8, 377—381).—Cases of severe diabetes are recorded in which small doses of levulose produced a great rise in the excretion of sugar, greater than that due simply to the dose given. Hence Külz's statement that diabetics are tolerant of levulose is not universally true. The use of *Syzygium Jambolanum* and piperazine in diabetes gave good results.

W. D. H.

**Excretion of Acetone, Diacetic acid, and  $\beta$ -Hydroxybutyric acid in Diabetes.** By W. WEINTRAUD (*Chem. Centr.*, 1894, ii, 891—892; from *Arch. exp. Path. Pharm.*, 34, 169—184).—The separation of these substances from the body is regarded as due to deficiency of oxidative processes. In the normal state, they are easily burnt off as carbonic anhydride. They may be regarded either as intermediate products of normal metabolic processes, or may, on the other hand, be due to a quantitative alteration in nutritional exchanges. This question is not yet ripe for settlement. Recent workers regard proteïd matter as the source of these three substances; but in the present research no evidence to support this view is derived from investigations on nitrogenous metabolism. The presence of hydroxybutyric acid in the urine should lead one to expect diabetic coma; and there is no parallelism between the excretion of this substance and that of acetone; as the acid diminishes, acetone does not increase; this is against the hypothesis that the acid is the source of acetone. The administration of sodium carbonate increases the acetone in the urine, but without correspondingly lessening the hydroxybutyric acid. Administration of organic acids including optically inactive hydroxybutyric acid increases these substances in the urine, but does not influence the

acetonuria. Carbohydrate diet markedly lessens acetonuria ; so does glycerol, as Hirschfeld showed first. Glycerol has a similar effect on the excretion of hydroxybutyric acid, but it increases the glycosuria.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effect of Oxygen on Alcoholic Fermentation.** By D. IWANOWSKY (*Bied. Centr.*, 1895, **24**, 120—121; from *Bot. Centr.*, 1894, **58**, 344).—A pure cultivation of beer yeast showed the same fermentative energy in presence of oxygen as in absence of oxygen.

A sugar solution was dropped at the rate of six or seven drops per minute on to yeast spread on a porous plate, the excess of solution passing through the plate into a vessel containing salicylic acid. The energy of fermentation was increased. But this was due to the continual removal of the alcohol, which, when present, hinders fermentation, and not to increased aëration. Similar experiments, conducted in oxygen and in nitrogen respectively, gave the same energy of fermentation.

The fermentative energy of yeast cells is, therefore, not influenced by oxygen, and no amount of aëration will enable the cells to respire like aërobic organisms; in this respect, there is an essential difference between yeast and the higher plants.

N. H. J. M.

**Alcoholic Fermentation.** By N. v. CHUDIAKOW (*Bied. Centr.*, 1895, **24**, 122—128; from *Landw. Jahrb.*, 1894, **23**, 391).—Fermentation in pure dilute sugar solution in presence of air is not lasting. In cases where fermentation continues, a portion of the yeast dies and changes the composition of the substratum; fermentation is accompanied with increase of yeast cells. The cessation of fermentation and dying off of the yeast cells is generally quicker at higher temperatures.

Fermentation in pure sugar solution is about 3·5 times more favourable in absence of air than in presence of oxygen. Oxygen does not assist fermentation as Nägeli maintains (*Theorie d. Gährung*, 1879), but makes it impossible (in pure sugar solution). The better the nutritive solution, the less is the unfavourable effect of oxygen, until with worts and peptone, oxygen has no effect at all (compare Iwanowsky, preceding abstract).

For the multiplication of yeast cells, oxygen is necessary when the nutritive solution is poor, but is almost unnecessary when sugar-peptone solution and worts are employed. This is in confirmation of Nägeli's and Mayer's results. In the experiments recorded, oxygen was in every case unfavourable to fermentation when necessary for multiplication; in all solutions, for instance, in which nitrogen was present in the form of ammonium salts. When, on the other hand, oxygen is not required for multiplication, it also is without injurious

effect on fermentation. The reasons of this relation between multiplication and activity as ferment seems to be connected with the nitrogen change in the yeast cells.

The activity of yeast as ferment rises with increase of temperature up to  $45^{\circ}$ , at which temperature the cells are killed. The presence or absence of oxygen is immaterial.

Apparent intramolecular respiration only occurs when yeast contains bacteria, or when the yeast cells still contain sugar. There is no intramolecular respiration in yeast, which in this respect resembles the moulds.

N. H. J. M.

**Albuminous Fermentation.** By FRITZ OBERMAYER and RICHARD KERRY (*Chem. Centr.*, 1894, i, 825; from *Centr. Physiol.*, 7, 806).—Yeast was mixed with water and partly inoculated with a few drops of decomposing blood, partly with fresh fæces, and then allowed to remain at the propagating temperature for 10—14 days. From the acid liquid thus obtained the yeast cells were precipitated by the addition of barium hydroxide and zinc sulphate. By Baumann and Udraňsky's method, from  $2\frac{1}{2}$  kilos. of yeast, 60 grams of dibenzoyldiamines were obtained and identified as the dibenzoates of putrescine and cadaverine. From the filtrate of these dibenzoates, a new benzoate,  $C_{28}H_{29}N_3O_5$ , was obtained by extraction with ether. This melts at  $117-118^{\circ}$  and is soluble in hot water, alcohol, ether, and benzene, insoluble in petroleum and carbon bisulphide. The liquid, after extraction with ether, was treated with sulphuric acid to free it from benzoic acid, neutralised with barium or calcium carbonate, and evaporated. The residue, after treatment with sulphuric acid, gave, when extracted with ether, the usual fatty acids, and a compound,  $C_{27}H_{30}N_4O_6$ , which melts at  $122.5^{\circ}$  and yields a soluble sodium salt melting at  $126-127^{\circ}$ . The above compounds,  $C_{28}H_{29}N_3O_5$  and  $C_{27}H_{30}N_4O_6$ , each contain three benzoyl groups, and are probably derivatives of heptonic and caproic acids. Egg-albumin, peptone, and gelatin yield the above compounds in small quantities. Yeast when treated with *Bacterium coli* did not yield diamines, and with *Bacillus proteus*, very small quantities only. Diamines are not formed either by boiling yeast with acids, or by melting albumin with potassium hydroxide.

E. C. R.

**Assimilation of Free Atmospheric Nitrogen by Microbes.** By SERGEI WINOGRADSKY (*Arch. Sciences Biol.*, 1895, 3, 297—352).—By means of "elective" cultivation—that is under conditions as exclusive as possible—a butyric ferment, which has the power of fixing free nitrogen, was isolated from other soil organisms. For this purpose, a nutritive solution was employed containing, besides mineral food, 2 to 4 per cent. of dextrose, prepared by Soxhlet's method, and quite free from nitrogen. Various moulds and small bacteria, &c., which seemed to be superfluous, were destroyed by heating for 10 minutes at  $75^{\circ}$ .

As regards the relation between sugar decomposed and nitrogen fixed, for every gram of sugar, the amount of nitrogen was about 2.5 to 3 milligrams—that is, under the conditions of the experiments. With increased amount, or perhaps greater concentration of sugar,

there seems to be less nitrogen fixed. There is also less fixation with imperfect aëration. The presence of a small amount of ammonia in the cultivations had either the effect of accelerating the fermentation at first, or it had no effect, according to the conditions. Larger amounts of ammonia (about 8 milligrams) reduced the fixation, whilst twice that amount checked fixation almost entirely.

The microbe, which is called *Clostridium Pasteurianum*, could not be identified with any known ferment, but morphologically it most resembles Prazmowski's *Clostridium butyricum*. The nitrogen which is fixed is mainly in an insoluble, organic form. The liquid products of the fermentation are chiefly butyric, with some acetic acid, whilst the gas evolved consists of hydrogen (60—75 per cent.) and carbonic anhydride. The quickest and surest way of isolating the microbe was to introduce a trace of soil into the saccharine solution (free from combined nitrogen) and to pass nitrogen through it; after making three to five passages in the same medium, the spores are heated for a quarter of an hour at 80°; finally, strictly anærobic potato cultures are made.

Pure cultivations of *Clostridium* do not give cultivations in gelatin or broth, which are too nitrogenous.

The methods employed in the investigation are fully described, and the results given in tables.

In conclusion, two series of experiments are described which were made in order to see whether other nitrogen-fixing organisms could be obtained from soil, Berthelot having stated that there are organisms of very different kinds, especially certain soil bacteria, which have this power. The results of the experiments, which were made under a variety of conditions, show that none of the 15 microbes obtained fixed nitrogen to an appreciable extent; *Clostridium* alone, as before, was found to be able to assimilate nitrogen. The microbes were, moreover, unable to utilise the carbohydrate in absence of combined nitrogen. In potato cultivations, two microbes, which were able in presence of combined nitrogen to assimilate very slight amounts of nitrogen, were obtained.

The power of fixing nitrogen does not therefore seem to be at all general among microbes, and is probably a quite specific function; and the ability to exist without combined nitrogen also seems to be possessed by *Clostridium* alone.

N. H. J. M.

**Alumina in Plants.** By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1895, **120**, 288—290).—Roots of lucern contain 0·45—0·5 per cent. of alumina, those of convolvulus 0·4 per cent., those of couch grass 0·12 per cent.; these quantities being of the same order as those of other metallic oxides. The alumina is associated with phosphoric acid. The leaves of lupin, on the other hand, contained only 0·037 per cent., and those of the lime only 0·0025 per cent., hence it would seem that the greater part of the alumina is arrested in the roots, and it is noteworthy that the plants containing marked quantities of alumina have abundant and deep roots. Aluminium phosphate and alumina can dissolve, and hence can be absorbed, in presence of citric, tartaric, and similar acids.

C. H. B.

**Carbohydrates of the Gum of *Acacia Decurrens*.** By WINTHROP E. STONE (*Amer. Chem. J.*, 1895, **17**, 196—199).—The gum of *Acacia decurrens* contains a complex carbohydrate of the galacto-araban character, and does not differ essentially from gum-arabic, peach-gum, or cherry-gum.  
A. G. B.

**Basswood Oil.** By F. G. WIECHMANN (*Amer. Chem. J.*, 1895, **17**, 305—308).—The author has examined two specimens of basswood (*Tilia Americana*), from Saginaw, Michigan. (1) Sound wood, (2) wood which had been kept in water for some time, and certain constituents of which had undergone decomposition. On extracting the powdered wood, oils were obtained which greatly resembled cottonseed oil. The oils are apparently glycerides, as on hydrolysing with potash they yield glycerol and a mixture of fatty acids (mainly butyric).  
J. J. S.

**Sap of the Lac Tree.** By GABRIEL BERTRAND (*Bull. Soc. Chim.*, 1894, [3], **11**, 717—721).—See this vol., i, 385.

**Moâbi Seeds.** By H. LECOMTE and ALEXANDRE HÉBERT (*Compt. rend.*, 1895, **120**, 374—377).—The moâbi is a large tree, which grows in parts of the French Congo; its very thick bark yields a milky juice, containing a somewhat large proportion of gutta percha. Its seeds closely resemble those of *Tieghemella Heckelii* (Pierre), and are 50 mm. long, 30 to 35 mm. broad, and 25 mm. thick; they consist of a kernel enclosed in an integument about 1 mm. thick.

One hundred parts of decorticated seeds consist of 36 parts of rind and 64 parts of kernel. The former contains small quantities of nitrogenous compounds and fat; the latter contains, after removal of the fat by benzene, ash, 4.40 per cent.; total nitrogenous compounds, 12.81 per cent. (nitrogen 2.05 per cent.), sugars 4.07 per cent., extractive matters 13.43 per cent., cellulose 18.75 per cent., resin 12.36 per cent.; it is therefore valuable as a manure or cattle food.

The fat is yellowish, melts at 32—33°, and solidifies at 25—26°; sp. gr. at 30° (liquid) = 0.894. It yields 88 per cent. of white, fatty acids melting at 45—46°, and containing about equal parts of liquid and solid acids. The liquid acid is oleic acid; the solid acids consist mainly of palmitic and stearic acids, with probably some myristic and margaric acids.  
C. H. B.

**Peculiar Property of Phosphoric acid in Peaty Soil.** By BRUNO TACKE (*Bied. Centr.*, 1895, **24**, 82—84; from *Mitt. d. Ver. z. Förd. d. Moorkultur.*, 1894, No. 21).—It was noticed that when peaty soils, on which crops fail unless manured with phosphates, are left for some years and become dried up, they will then generally give good yields without phosphate manuring. Experiments are described in which plants were grown in pots containing peaty soil manured with lime, kainite, and sodium nitrate. The soil was used (1) in its original state, (2) after being dried at 50°, (3) dried at 100°, and (4) dried at 180°. The results, showing amount of produce, phosphoric acid in dry produce, and total phosphoric acid removed per pot, are given in a



table. By drying at a low temperature, about four times as much produce was obtained as in the fresh soil, whilst the percentage of phosphoric acid in the produce was nearly doubled. The soil dried at  $180^{\circ}$  gave less produce than the soil dried at  $50^{\circ}$ ; but the percentage of phosphoric acid was more than twice as high. Whilst the soil in its original state only gave up 1.8 per cent. of its phosphoric acid, the soil dried at  $180^{\circ}$  gave up nearly 20 per cent.

It is suggested that the greater availability of the phosphoric acid in the soils which had been dried may be due (1) to the liberation of phosphoric acid from organic phosphorus or phosphatic compounds, (2) to the destruction of so-called colloïd substances which held back the phosphates, and (3) the formation (with or without co-operation of oxygen) of strongly acid compounds which decomposed insoluble phosphoric acid compounds present in the soil.

N. H. J. M.

**Loss of Nitrogen in Drainage Waters.** By J. J. THÉOPHILE SCHLOESING (*Compt. rend.*, 1895, **120**, 526—530).—With a view to estimate the actual loss of nitrogen in drainage waters that have percolated through the soil, the author determined the quantities of nitrates present in the water of the Seine at three different points, in the water of its chief tributaries, and in the spring waters supplied to Paris. The determinations were made during the past severe winter, after the temperature had been below  $0^{\circ}$  for some weeks, and under these conditions it may be assumed that there was no surface drainage, and that the activity of aquatic vegetation of all kinds was so reduced that its influence on the quantity of nitrates may be neglected. The results in milligrams of nitrogen per litre are as follows.

*Water of the Seine.*

	Paris.				Montereau.		Charenton.	
Feb.	9th.	13th.	19th.	23rd.	16th.	17th.	15th.	28th.
	2.09	2.31	2.25	2.26	1.99	2.08	2.55	2.75

The Marne at Charenton gave 2.34 on February 14 and 2.02 on February 28 the Yonne at Montereau, 2.21 on February 16 and 2.52 on February 27; the Oise at Pontoise, 2.78 on February 19 and 2.43 on March 1; whilst the spring waters from Vanne, Dhuis, and Avre gave 2.61, 2.86, and 3.08 respectively.

The constancy of the proportion of nitrates in the Seine and its tributaries from February 14 to February 28 is remarkable, and this proportion remained constant in spite of the considerable diminution in the quantities of water flowing down the rivers.

Calculating on the basis of the volume of water flowing down the rivers, and allowing for the fact that part of the basin of the Seine is occupied by woods, meadows, moors, &c., it is found that the loss of nitrogen per hectare is 4.2 kilos. if the layer of infiltrated water is taken as one-sixth of 700 mm. (the mean rainfall), 6.44 kilos. if it is taken as one-fourth of 700 mm., and 8.48 kilos. if it is taken as one-third of 700 mm. These losses are much smaller than has hitherto been supposed, and it is noteworthy that the loss will be smallest in

poor soils, and highest in rich soils, in which the high proportion of organic matter and the activity of nitrification will soon make up the loss.

C. H. B.

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## Analytical Chemistry.

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**Universal Gas Volumeter.** By GEORG LUNGE (*Bull. Soc. Chim.*, 1894, [3], 11, 625—650).—A self-correcting modification of the well-known nitrometer. The gas to be measured is in most cases generated or treated in a separate vessel, and transferred to the measuring apparatus. This consists of three vertical tubes, which can be moved up and down independently, and are connected at the lower ends by flexible tubing. The graduated measuring tube communicates through a two-way tap with the generating and absorption vessels, and is enlarged by a bulb at the middle; the second tube is open at the top, and serves to regulate the pressure of the gas; the third, or reduction tube, is filled with an amount of air which, if dry, would occupy 100 c.c. at the standard temperature and pressure. When the mercury is at the same level in the measuring and reduction tubes, and the air in the latter occupies 100 c.c., the gas in the measuring tube occupies the volume it would occupy when dry at the standard temperature and pressure. By suitably altering the amount of air in the reduction tube, any desired set of readings may be made in the measuring tube, as, for instance, the weight of a particular gas. Means are provided for introducing a drop of water or sulphuric acid into the measuring tube.

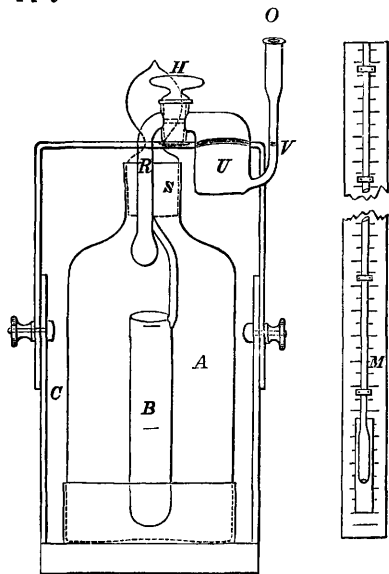
The apparatus is applicable to all purposes for which the nitrometer is available. In estimating the value of bleaching powder, manganese dioxide, and permanganate, advantage is taken of the ready way in which these substances liberate oxygen from hydrogen peroxide. The nitrogen of ammonia and of carbamide is liberated as such by alkaline hypobromite. Carbonic anhydride in carbonates may be liberated in the generating vessel, and expelled into the measuring tube by hydrogen generated from aluminium in the same vessel, the amount being measured by absorption with alkali. Carbon in iron is estimated in the same way, the iron being first dissolved by copper sulphate, and the resulting mixture of copper and carbon oxidised with chromic acid. Different forms of generating vessels are described for these various purposes.

The measuring tube may be connected with a V. Meyer vapour density apparatus, and the density determinations can then be made under reduced pressure. The apparatus may also be used as a barometer.

JN. W.

**The Gasgravimeter.** By GUIDO BODLÄNDER (*Zeit. angew. Chem.*, 1895, 49—55).—The apparatus differs from the author's gasbaroscope by its simpler construction and manipulation; also by the very small

quantity of mercury required. It is suited for a large number of analyses, such as the estimation of carbonates by means of acids, and of acids by means of calcium carbonate, the valuation of zinc dust by means of hydrochloric acid, the estimation of urea by alkaline hypobromite, &c., in fact in all analyses where it is not necessary to apply heat, and where no nitric oxide is being evolved.



The gasgravimeter (see illustration) consists of a 500 c.c. flask *A*, with which is connected the U-tube *UV* by means of the side tube *R* and stop-cock *H*. To the glass stopper *S*, which is closely ground in the neck of the flask, is sealed a 20—50 c.c. graduated beaker *B*. One arm *U* of the U-tube is closed on the top, and has a diameter of 20 mm. and an equal height; the other arm *V* has a diameter of 2 mm., and to its opening *O* is ground a tube *V'*, 50 cm. in length and 2 mm. in diameter, open at both ends. *V* has a mark at 1—2 cm. from the bend. *V'* is attached to an empirical or calculated scale *M* in such a manner that the zero of the scale corresponds with the

mark on *V* when *V'* is put on *V*. The apparatus is fixed in a support *C* in such a manner that when pressure occurs in *A* the stopper cannot possibly blow out.

When the apparatus is wanted for analysis, mercury is poured through *O* into the U-tube until its top in *V* corresponds with the mark on *V* when both arms of the U-tube are under the same pressure. The solid or liquid substance to be tested is now put in weighed or measured quantity on the bottom of *A*, and into the beaker *B* is put an excess of the decomposing reagent. The well greased stopper is now put on to the flask, which is then fixed in the support *M*; the stop-cock *H* is removed, and the apparatus is put into a large trough holding water of the temperature of the laboratory. After a few minutes the stop-cock *H* is put in so as to cut off the contents of the flask, the opening *O* is closed to prevent loss of mercury during the shaking, and by inclining the apparatus the reagent is allowed to run on to the sample. After the action has finished, the apparatus is again placed in the trough, the stopper from *O* is removed, and the tube *V'* placed on *V*. By cautiously turning the stop-cock *H* the extra gas pressure is gradually spread through *U*, and the mercury gradually rises in *V* and *V'*. The level of the mercury in *V* or *V'* is read off on the scale.

The quantity of gas evolved is proportional to the pressure of the

mercury column in  $V$  and  $V'$ , and may be directly ascertained without consulting the barometer by a simple calculation. L. DE K.

**Potassium Hydrogen Tartrate as Material for Standardising Alkalis.** By ARTHUR BORNTRÄGER (*Zeit. anal. Chem.*, 1894, **33**, 713—714).—The proposal of the author (Abstr., 1892, 525; 1893, ii, 144) and others to make pure potassium hydrogen tartrate the starting point for preparing standard alkalis was, as well as his method of purifying the salt (*loc. cit.*), adopted at a conference of the directors of Italian agricultural experimental stations held at Modena on December 27—28, 1893. M. J. S.

**Estimation of Bromine in Presence of Chlorine.** By WILHELM WENSE (*Zeit. angew. Chem.*, 1895, 13—14).—The author recommends the following process for estimating small quantities of bromine in brines. The solution is mixed with a slight excess of chlorine water, and distilled into a solution of potassium iodide of known strength. When all the bromine has distilled over, this solution is made up to a convenient bulk, and the liberated iodine is titrated in an aliquot part by means of sodium thiosulphate. Another portion is carefully evaporated in a tared dish, dried at 160—180°, and weighed. The process is based on the fact that 1 milligram of bromine acting on an iodide causes a loss in weight of 0.5866 milligram, whilst 1 milligram of chlorine causes a loss of 2.5773 milligrams. If now  $T$  represents the amount of liberated iodine, and  $D$  the loss in weight of the potassium iodide,  $c$  the amount of chlorine, and  $b$  the amount of bromine in the sample, the calculation will be

$$\begin{aligned} 1. \quad T &= c + b + D. \\ 2. \quad D &= 0.5866 b + 2.5773 c. \end{aligned}$$

$$\begin{aligned} \text{or} \quad c &= 0.797 D - 0.295 T. \\ b &= 1.295 T - 1.797 D. \end{aligned}$$

The test analyses are satisfactory.

L. DE K.

**Colorimetric Estimation of Hydrogen Sulphide.** By A. C. HUYSE (*Chem. Centr.*, 1894, ii, 108; from *Nederl. Tydschr. Pharm.*, **6**, 167—171).—The method depends on the formation of methylene blue. One c.c. of hydrochloric acid (30 per cent.), four drops of paramidodimethylaniline hydrochloride solution (2 per cent.), and five drops of ferric chloride solution (0.5 per cent.) are added to 50 c.c. of the solution containing the hydrogen sulphide. The limits of applicability of the process are 0.48 milligram and 0.01 milligram of hydrogen sulphide per 100 c.c. of water; hence it is serviceable in the examination of natural waters. A. G. B.

**Estimation of Tellurium in Copper Bullion.** By CABELL WHITEHEAD (*J. Amer. Chem. Soc.*, 1895, **17**, 280—281).—Twenty to fifty grams of the bullion is dissolved in nitric acid (sp. gr. 1.286) and the excess of acid is then boiled off. To the solution is added a solution of ferric nitrate, equivalent to 0.25 gram of iron. The hot solution

is precipitated with excess of ammonia, and the precipitate is washed with dilute ammonia until free from copper; redissolving and reprecipitating if necessary. The precipitate which contains the tellurium and selenium as ferric compounds is dissolved in hydrochloric acid, mixed with excess of tartaric acid, and rendered alkaline with aqueous potash; on passing hydrogen sulphide, the tellurium and selenium dissolve as double sulphides. They are then precipitated from their alkaline solution by means of hydrochloric acid, and redissolved in nitro-hydrochloric acid. The solution is evaporated to dryness; the residue is dissolved in hydrochloric acid and then precipitated by a current of sulphurous anhydride. After first weighing the joint tellurium and selenium on a filter, the latter is extracted by boiling with concentrated solution of potassium cyanide and then reprecipitated by addition of hydrochloric acid. The filtrate contains a small amount of tellurium, which may be recovered by precipitating with sulphurous acid.

L. DE K.

**Kjeldahl's Method and Platinochlorides.** By MARCEL DELÉPINE (*Compt. rend.*, 1895, 120, 152—153).—Trimethylamine platinochloride, when subjected to Kjeldahl's process, gave only 3.88 per cent. of nitrogen instead of 5.15; and ammonium platinochloride gave only 1.89 per cent. instead of 6.26. This loss of nitrogen is in all probability due to the action of the chlorine of the platinochloride on the ammonia or the amine, the nitrogen being liberated.

C. H. B.

**Volumetric Estimation of the Soluble Phosphoric Acid in Superphosphates.** By WILHELM KALMANN and K. MEISSELS (*Zeit. anal. Chem.*, 1894, 33, 764—766; from *Mitt. tech. Gewerbemuseums*, Wien, 1894).—Twenty grams of the superphosphate is dissolved to one litre. (a) 100 c.c. of the filtered solution, coloured with methyl-orange, is accurately neutralised with seminormal alkali. Phenolphthaleïn is then added, and the amount of alkali required to produce the pink colour is noted. (b) 100 c.c. of the solution is mixed in a 250-c.c. flask with a moderate excess of seminormal alkali, made up, shaken, and filtered from the precipitated tricalcium phosphate. One hundred c.c. of the filtrate is mixed with phenolphthaleïn and neutralised with seminormal acid. Methyl-orange is then added, and the amount of acid required to produce the change of colour is ascertained. Titration (b) gives a result which is exactly as much too low as that of (a) is too high. The arithmetical mean, multiplied by 0.0355, gives the amount of phosphoric anhydride in 2 grams of the substance. The results agree closely with those of the citrate method.

M. J. S.

**Analytical Communications.** By FR. SCHEIDING (*Zeit. angew. Chem.*, 1895, 79—81).—*Sources of error in alkalimetry.*—The author has proved by a series of experiments that the excess of normal soda often required to neutralise a known quantity of acid is solely due to the presence of carbonic anhydride. In titrating with phenolphthaleïn as indicator, the apparently neutralised solution should be again acidified with about 0.2 c.c. of standard acid, boiled for 10

minutes, and then again be titrated with the alkali. As regards methyl-orange, the author states that this indicator is indifferent to small quantities of carbonic anhydride but is slightly affected by large amounts. The notion that it can only be used in cold liquids is erroneous, as it acts quite as well in hot solutions.

*Estimation of phosphoric acid.*—The precipitate obtained in the citrate method generally gives, on ignition, a black mass. The author advises moistening it with solution of ammonium nitrate, when a snow white residue will be finally obtained. When bone-meal is digested with sulphuric acid to dissolve out the phosphoric acid and also the nitrogenous matter, an insoluble residue is left which, as a rule, is not filtered off but introduced into the measuring flask. The author has found that when using 5 grams of the sample the insoluble residue may be taken to occupy 1.5 c.c., and in accurate analysis allowance should be made for this.

*Reduction of ferric salts by means of zinc, prior to titrating with permanganate.*—The iron solution should be very dilute, containing no more than 0.15 gram of iron per 250 c.c. Not less than 20 grams of zinc and 30–50 c.c. of sulphuric acid should be added, and after this has been acting for 5–6 hours the whole should be boiled, with exclusion of the air. If these precautions are not taken, the results will be quite untrustworthy. L. DE K.

**Estimation of Sulphur in Pyrites.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1895, 69–73).—The author's method consists in treating the sample with nitro-hydrochloric acid and precipitating the sulphuric acid with barium chloride, after having first removed the iron by precipitating with ammonia. Gladding has stated that it is better to oxidise the ore with bromine and nitric acid, and also that the ferric hydroxide retains sulphuric acid which must afterwards be estimated by barium chloride.

The author states that his original nitro-hydrochloric acid method is better than the bromine process; also that when working according to his directions, no sulphuric acid is retained by the iron precipitate (compare Abstr., 1893, ii, 187). L. DE K.

**Estimation of Zinc.** By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1895, 17, [4], 310–312).—About 0.8 gram of zinc ore is dissolved in hydrochloric acid; but as any insoluble residue may still contain *spinel*, it must be examined separately by fusion. The acid solution is evaporated to dryness, the residue redissolved in nitric acid (sp. gr. 1.2), again evaporated to moist dryness, 100 c.c. of strong nitric acid added, and the manganese precipitated by means of potassium chlorate. The liquid, after being filtered through asbestos and the precipitate washed, first with nitric acid and then with water, is evaporated to dryness, taken up with hydrochloric acid and again evaporated to dryness. After dissolving in water, the usual double basic acetate precipitation is made. The zinc is first precipitated by a current of hydrogen sulphide, and after being redissolved in hydrochloric acid is precipitated as zinc ammonium phosphophosphate, which is finally ignited and weighed as zinc pyrophosphate. L. DE K.

**Chemical Investigation of Steel.** By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1894, ii, 112—113; from *Österr. Zeit. Berg. u. Hüttenwesen*, 42, 241—244; compare *Abstr.*, 1893, ii, 392).—To estimate the carbide-carbon in steel, 2 grams of the steel is dissolved in 100 c.c. of dilute sulphuric acid (1 : 10) with exclusion of air; the residue is filtered, and the carbon in it is burnt in the usual manner. To estimate the total carbon, the sample is dissolved in sodium cupric chloride solution in the usual way, the author preferring to prepare the solution by boiling 1 kilo. of cupric sulphate with  $\frac{3}{4}$  kilo. of sodium chloride in 2 litres of water, and decanting the boiling hot solution from the separated sodium sulphate; the cooled liquid is ready for use.

It is impossible to directly burn the carbon in a steel because of the protective layer of iron oxide which forms on the metal. But if a mixture of powdered iron, powdered lead, and powdered copper be heated to a low redness, and oxygen be passed over the mixture, the lead and copper burn and effect the complete oxidation of the iron. Lead powder is obtained by shaking molten lead until it is cold; copper powder is prepared by heating fine copper wire and reducing the oxide in hydrogen, the product being afterwards easily powdered; the two powders are mixed in the proportion of three of lead to one of copper. The steel can be obtained in sufficiently small particles by the prolonged hammering of the borings in a steel mortar; the very thin plates thus obtained will burn equally as well as powdered iron. Three grams of the finely-divided steel are mixed with 10 grams of the copper-lead mixture, and disposed in a porcelain boat, which rests on a mat of ignited asbestos in a combustion tube. The front part of the tube contains a column of copper oxide some 10—20 cm. long, and the combustion is effected in the usual manner in oxygen. A blank experiment with the copper-lead mixture is necessary. The results are from 0.01 to 0.2, average 0.04, per cent. higher than those yielded by the sodium cupric chloride method.

It is noted that in the process of subdividing the steel mentioned above, a portion of the material falls to very fine powder at the beginning of the hammering, but that this tendency rapidly diminishes as the hammering is continued. The proportion between spangles and powder obtained from various specimens has been approximately determined, since it must have some connection with the tenacity of the sample. The following figures give the percentage proportion of spangles to powder. Nickel-steel, 99 : 1; Krupp's tool steel, 98 : 2; crude puddled steel, 94 : 6; chrome-steel, 90 : 10; rolled steel, 78 : 22; Martin ingot iron, 69 : 32 and 68 : 40; puddled steel, 66 : 34; crucible cast steel, 32 : 68; tungsten-steel, 5 : 95; Mushet steel, 0 : 100.

A. G. B.

**Barium Hydroxide Solution in Steel Analysis.** By JAMES O. HANDY (*J. Amer. Chem. Soc.*, 1895, 17, 247—251).—When estimating carbon in steel, the author prefers passing the dried products of combustion through a 2 per cent. solution of barium hydroxide. The absorption apparatus consists of two tubes, each consisting of a long, slanting tube connected at both ends with a bulb. The precipitated barium carbonate may be collected and



weighed, and in this case a current of air free from carbonic anhydride is passed over the surface of the liquid so as to prevent the formation of a film of carbonate during the filtration. Or the excess of barium hydroxide may be titrated, best with standard sulphuric acid, as in Pettenkofer's method of air analysis.

L. DE K.

**Estimation of Free Ferric Oxide in Soil.** By ROBERT SACHSSE and ARTHUR BECKER (*Landw. Versuchs-Stat.*, 1895, **45**, 419—422).—The process consists in first converting the ferric oxide into sulphide, and this, by means of potassium cyanide, into potassium ferrocyanide. The substance is mixed with water (about 100 c.c.), treated with potassium cyanide (3 grams) and with hydrogen sulphide for an hour. The excess of hydrogen sulphide is expelled by heating on a water-bath, after which the whole is filtered. The filtrate is strongly acidified with sulphuric acid, evaporated to dryness, and ignited. The residue is redissolved and titrated, as usual, with permanganate.

With precipitated ferric hydroxide mixed with kaolin, very good results were obtained, but with the natural crystalline oxides the results were less satisfactory. In the case of brown hæmatite not much more than half was dissolved, and lepidokrokit behaved similarly; a single sample of göthite gave three different results. The incomplete solution is due to the fact that crystalline ferric hydroxide is scarcely converted into sulphide by hydrogen sulphide. Experiments, in which precipitated ferric hydroxide was treated with hydrogen sulphide at the ordinary temperature and at 100°, showed an increase of weight corresponding nearly with, or even exceeding, that required by  $\text{FeS}_2$ ; in one case (at 100°), the product had almost exactly the weight corresponding with the formation of  $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{S}$ . Göthite, when similarly treated, scarcely increased in weight at all, whilst brown hæmatite behaved like a mixture of amorphous and crystalline ferric oxide (compare Abstr., 1893, ii, 243).

N. H. J. M.

**Estimation of Iron and Aluminium in Phosphates.** By K. P. McELROY (*J. Amer. Chem. Soc.*, 1895, **17**, 260—263).—The method given by Ogilvie (wrongly known as the McElroy process) consists in neutralising the filtrate from the molybdic precipitate with ammonia. The iron and aluminium precipitate is redissolved in acid and reprecipitated by ammonia, washed, dried, and weighed. The author has obtained good results by this method, but of late has become convinced that the process is untrustworthy.

L. DE K.

**Separation of Nickel from Iron.** By EDWARD D. CAMPBELL and W. H. ANDREWS (*Amer. Chem. J.*, 1895, **17**, 164—167).—The mixed metals are dissolved in nitric acid, which is used to the extent of 20—25 c.c. in excess, and a solution of sodium pyrophosphate (13 grams to each gram of metal) in warm water is added. The precipitated ferric pyrophosphate is then just dissolved by adding a moderately strong solution of sodium carbonate until the liquid has a dull olive-green colour. If excess of the carbonate be

employed, the subsequent precipitation of the nickel will be incomplete. The solution is filtered through asbestos into a flask, and the nickel precipitated as xanthate by adding a fresh cold concentrated solution of potassium xanthate. The flask is stoppered, and shaken intermittently for 10 minutes to complete the precipitation. The xanthate is filtered through asbestos, washed with a 1 per cent. solution of potassium xanthate, and dissolved in nitric acid (1 : 1) freshly diluted. Dilute sulphuric acid (2 c.c.) is then added, and the solution boiled down until fumes of sulphuric acid are evolved. The residue is dissolved in water, and the iron precipitated by a small excess of ammonia; the ferric hydroxide must be redissolved and reprecipitated; it seldom exceeds 0.003 gram. The ammoniacal solution is transferred to a large platinum dish (200 c.c.), a solution of disodium hydrogen phosphate (3 grams) is added, together with 25 c.c. of strong ammonia, and the nickel is deposited electrolytically by a current of 0.14 ampère per 100 sq. cm. of the dish, for 12 hours. An alternative method is to titrate the slightly ammoniacal filtrate from the ferric hydroxide with a standard solution of potassium cyanide, using silver nitrate, followed by potassium iodide, as an indicator; the suspended silver iodide will only dissolve when all the nickel has been converted into potassium nickel cyanide.

A. G. B.

**Estimation of Chromium in Chrome Ore.** By EDMUND CLARK (*J. Amer. Chem. Soc.*, 1895, **17**, 327—330).—0.5 gram of the finely-ground sample is weighed into a 50-c.c. platinum crucible, covered with 25 grams of potassium hydrogen sulphate, and fused over a Bunsen burner protected from draughts; the heat being gradually increased to prevent sputtering, and finally kept at a moderate red heat for 40 minutes. The contents are poured into a platinum dish, and, when cold, boiled with 35 c.c. of hydrochloric acid and 25 c.c. of water; the liquid is then introduced into a beaker, into which has been placed the crucible and its cover, to dissolve the remainder of the sulphates. After settling, the clear liquid is decanted, and the residue treated with another 15 c.c. of acid; finally, the liquid is filtered, ammonia added in slight excess, and the mixture heated until the odour of ammonia is scarcely perceptible. The precipitate, freed from lime and magnesia by redissolving it in hydrochloric acid and reprecipitating with ammonia, is dissolved in 50 c.c. nitric acid (sp. gr. 1.42), heated over a Bunsen flame, and from time to time *small* quantities of potassium chlorate are added, the gradual oxidation being accompanied by a change of the green colour to a clear orange-red; a little more chlorate is added to insure complete oxidation. The iron and alumina are now separated from the chromic acid by means of ammonia, but to render this complete, the precipitate must be redissolved in nitric acid and reprecipitated by ammonia; the united ammoniacal filtrates contain all the chromic acid, from which it may be easily precipitated as chromic hydroxide by adding hydrochloric and sulphurous acids and then ammonia. Or the liquid may be acidified with acetic acid, precipitated by lead acetate, and the chromium

weighed as lead chromate. The process admits of the accurate estimation of the iron and other impurities in the ore.

L. DE K.

**Assay of Alloys containing Gold, Silver, Zinc, and Tin.** By RICHARD OEHMICHEN (*Zeit. angew. Chem.*, 1895, 133).—The author has tabulated the results of 22 experiments, showing that the direct cupellation of these alloys gives results considerably below the truth.

L. DE K.

**Improved Methods of Water Analysis.** By IRVING A. BACHMAN (*J. Amer. Chem. Soc.*, 1895, 17, 296—303).—The author has noticed that, when using the albuminoid ammonia process, the evolution of ammonia is often increased as the liquid in the retort becomes more concentrated. Acting on this observation, the new apparatus is so arranged that the 50 c.c. permanganate solution acts on 50 c.c. of water only, and when 30—40 c.c. has distilled over, the remaining 250 c.c. of water is allowed to run in at the same rate as the distillation is proceeding, which must not exceed 15 c.c. in 15 minutes. The distillation is stopped when 250—300 c.c. has passed over. Before adding the permanganate, the water (500 c.c.) is, of course, freed from saline ammonia by distilling with sodium carbonate until 300 c.c. is left.

The apparatus consists of a distilling flask connected with two burettes with stop-cocks, the smaller one of which admits the solution of sodium carbonate and afterwards the permanganate, whilst the larger one serves to draw up the water after the free ammonia has passed over. The cooling apparatus is a closely coiled glass worm, with a long projection at the lower extremity, to which is attached a vessel by a soft rubber stopper, which is in turn connected with a nitrogen bulb filled with Nessler solution. By means of an air-pump, a partial vacuum may be established. The distilling flask is heated in a brine bath. If the directions are properly adhered to, the condensation will be very complete, and no discoloration will be noticeable in the Nessler solution.

The author has obtained good results with the organic carbon process, but prefers to evaporate the water in a vacuum, to avoid the objectionable features of open-air evaporation.

L. DE K.

**Composition of American Peppermint Oil.** By FREDERICK B. POWER and CLEMENS KLEBER (*Zeit. anal. Chem.*, 1894, 33, 762—763).—The oil prepared by the authors from the fresh plant contains acetaldehyde, valeraldehyde, acetic acid, isovaleric acid, pinene (inactive?), phellandrene, lœvolimonene, cineole, menthone, menthol, menthylic acetate, menthylic isovalerate, the menthylic salt of an acid  $C_8H_{12}O_2$ , a lactone, and cadinene.

To estimate the menthol and menthone, 20 grams of the oil is freed from the ethereal salts by cohobating with 30 c.c. of normal alcoholic soda for an hour, after which the unconsumed soda is titrated by normal acid (using phenolphthaleïn). The well washed oil is then acetylated by boiling for an hour with an equal volume of acetic anhydride and 2 grams of anhydrous sodium acetate in a reflux apparatus. The product is washed with water and dilute soda, dried with calcium chloride, and filtered. Using 8—10 grams, the saponi-

fication number of this acetylated product is then determined, and the menthol calculated therefrom. Since 1 c.c. of normal soda corresponds with 0.156 gram of menthol, or 0.198 gram of menthylic acetate, for every 1 c.c. of soda consumed, the difference, 0.042 gram, must be subtracted from the weight of acetylated substance employed, in order to calculate the percentage of menthol in the unacetylated oil.

For estimating the menthone, a portion of the oil freed from ethereal salts is dissolved in twice its volume of alcohol and boiled with sodium. The oil is then precipitated by water; one half of it is used for a menthol estimation, and the menthone is calculated from the excess of menthol found. The other half is again treated with sodium to ascertain whether the reduction of the menthone had been complete.

The sp. gr. of the oil ranges from 0.905 to 0.916; the specific rotatory power from  $-25^{\circ}$  to  $-35^{\circ}$ . The menthol present as ethereal salts varies from 3.45 to 14.12 per cent.; the free menthol from 24.2 to 72.7 per cent.; normal American oil containing 40—50 per cent. Mitcham oil, and especially Japanese oil, are richer in menthol than American. In a specimen containing 54.5 per cent. of menthol (total), 12.3 per cent. of menthone was found.

M. J. S.

**Detection and Estimation of Alkyl Groups attached to Nitrogen.** By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1894, 15, 613—626; compare *Abstr.*, 1894, ii, 219).—The authors have carefully examined the method previously proposed (*loc. cit.*) for the estimation of alkyl groups attached to nitrogen, and, for the purpose, employ special apparatus, which they fully describe. The method, which depends on the fact that, when heated, the hydriodides of certain bases which contain alkyl groups attached to nitrogen yield the base and an alkylic iodide, can obviously be employed only for those substances which form hydriodides. In almost every case the expected results were obtained, but methylphenylhydrazine persistently gave a methyl number only half of that corresponding with its accepted constitution, whilst no methyl group could be recognised in sparteine and only one alkyl group was obtained from pilocarpin.

G. T. M.

**Influence of the Lead Acetates on the Estimation of Invert Sugar.** By ARTHUR BORNTAEGER (*Zeit. angew. Chem.*, 1895, 103—104).—The author has stated, two years ago, that large quantities of lead acetate or basic acetate interfere with the accurate estimation of invert sugar by the Fehling-Soxhlet process. Small quantities of these salts are, however, harmless.

The matter has been investigated by Edson, and also by Weld, but their method of working does not admit of comparison with the author's process.

L. DE K.

**Estimation of Cane Sugar in the Presence of Commercial Glucose.** By H. A. WEBER and WILLIAM MCPHERSON (*J. Amer. Chem. Soc.*, 1895, 17, 312—320).—The process used by the authors consisted in taking the sp. gr., specific rotatory power, copper

reducing power, and ash. They come to the following conclusions. 1. An error is introduced in the cane-sugar estimation by the presence of dextrin in commercial glucose, as this also undergoes a slight hydrolysis during the inversion of the sugar by acids. 2. That this error, however, may be reduced to a minimum if the inversion of the cane sugar is effected by heating for 10 minutes only, the temperature being gradually raised so as to reach  $68^{\circ}$  at the expiration of this time. 3. That the results with different glucoses are sufficiently uniform to warrant the introduction of a correction for the mean error. 4. That analysts should strictly adhere to one method of inversion.

L. DE K.

#### **Action of Acetic and Hydrochloric acids on Cane Sugar.**

By H. A. WEBER and WILLIAM MCPHERSON (*J. Amer. Chem. Soc.*, 1895, **17**, 320—327).—The authors have found that when hydrochloric acid is used for the inversion of cane sugar, the polariscopic reading is  $1.4^{\circ}$  too high, whilst, if acetic acid is used, the error is only  $0.2^{\circ}$ . This explains why it was formerly thought that acetic acid never caused complete inversion. Acetic acid, although acting very slowly, is preferable to hydrochloric acid, particularly when the sample contains dextrin, as it does not act on the latter.

L. DE K.

**Reaction of Hydroxycarboxylic acids.** By ARMAND BERG (*Bull. Soc. Chim.*, 1894, [3], **11**, 882—883).—Uffelman's reagent for lactic acid, namely, extremely dilute ferric chloride coloured amethyst by phenol, is more sensitive without the latter, and is of general application. The reagent should be slightly acid, the best proportions being two drops of ferric chloride solution and two drops of hydrochloric acid to 100 c.c. of water. An intense yellow colour is produced with the following  $\alpha$ - and  $\beta$ -hydroxy-acids, but not with methoxy- or ethoxy-isobutyric acids:—Malic, tartaric, citric, glycollic, lactic,  $\alpha$ -hydroxyisobutyric, glyceric, gluconic, mucic, phenylglycollic, and hydracrylic acids.

JN. W.

**Estimation of Salicylic acid and Salicylates.** By LEONCE BARTHE (*Bull. Soc. Chim.*, 1894, [3], **11**, 516—522).—The method described is applicable to the salicylates and benzoates of the alkalis, as well as to the salicylates of the alkaline earths and certain of the heavy metals, and is based on the non-volatility of salicylic acid with aqueous vapour at  $50$ — $60^{\circ}$ .

Sodium salicylate, for instance (1.6 grams =  $1/100$  gram-molecules), is dissolved in hydrochloric acid (2 c.c.) and water (20 c.c.), and the solution evaporated to dryness at  $50$ — $60^{\circ}$ ; the residue of salicylic acid and sodium chloride is then taken up with boiling water (50—60 c.c.), and titrated with alkali in presence of phenolphthalein. The amount of normal alkali in cubic centimetres multiplied by 10 gives the percentage of pure salt. The metal can be indirectly estimated in the same portion by titrating the chlorine with silver nitrate in presence of a chromate after the alkaline phenolphthalein has been decolorised with nitric acid. Ammonium

salicylate requires litmus, but the ammonia can be determined by the same indirect process in a separate portion. The acid may be estimated in manganese and bismuth salicylates after removing the base by means of sodium carbonate; the base, as oxide, by igniting the salt with ammonium nitrate. Mercuric salicylate is dissolved in potash, the solution acidified with hydrochloric acid, and evaporated to dryness at 40–45°; the residue of salicylic acid and mercuric chloride is then dissolved in a known excess of aqueous potassium iodide, and the acid titrated in presence of phenolphthaleïn. The mercury is estimated by titrating the excess of iodide with mercuric chloride.

The solubility of the various salicylates may be determined by estimating the acid in the saturated solution; that of the magnesium salt is 0.8015 gram per 100 c.c.; that of the strontium salt 1.830. Basic strontium salicylate,  $C_7H_4O_3Sr + 2H_2O$ , appears to be dissociated in solution into the normal salicylate and free alkali.

JN. W.

**Gaseous Products in Milk.** By WILHELM THÖRNER (*Chem. Zeit.*, 1894, 18, 1845–1848).—The author has estimated the amount of gaseous matters contained in a large number of milks of different age and composition, and tabulated the results. It appears that separated milk only retains 27–54 c.c. of gas per litre, whilst the fresh article generally has from 57 to 86 c.c., the deficiency being chiefly caused by loss of carbonic anhydride. Five or ten minutes' boiling is not sufficient to expel all the gases, the amount retained being 15–19 c.c. per litre.

The author states that the well-known taste of boiled milk is chiefly due to the great loss of gas, mostly carbonic acid, and that the original taste may be restored by cautious introduction of sterilised carbonic anhydride mixed with air.

L. DE K.

**New Process for Estimating Fat in Milk.** By P. FERNANDEZ-KRUG and WILHELM HAMPE (*Zeit. angew. Chem.*, 1894, 683–687, 709–710).—Five c.c. of milk is slowly dropped from an accurate pipette on to 7.5 grams of elutriated and ignited kaolin contained in a 200-c.c. nickel basin. After thoroughly mixing, 5 grams of powdered anhydrous sodium sulphate is added, and everything is again carefully mixed; the mass soon gets dry without application of heat, and is then introduced, by means of a nickel funnel and a little brush, into a 100-c.c. flask, which is fitted with a glass stopper or a clean cork. Twenty-five c.c. of pure ether is delivered from an accurate pipette, and the mixture is shaken for five minutes; after settling, 5 c.c. of the clear liquid is pipetted off, put into a 12-c.c. weighed glass flask, the flask placed on a hot metallic plate, and the vapour ignited; the last traces of ether are removed by a gentle blast, and the pure fat is then weighed. This method gives excellent results, as proved by numerous test experiments.

For the benefit of those who do not care to use an ordinary chemical balance, the authors have constructed a balance of the Westphal type, which allows the direct reading off of the percentage of fat.

L. DE K.

**Estimation of Fat in Milk.** By CARL BOETTINGER (*Chem. Zeit.*, 1894, 18, 1660).—The author introduces 6 c.c. of the sample of milk into a so-called butter-tester divided to 0.2 c.c., adds 1.2 grams of ignited amorphous silica, and shakes vigorously for five minutes. The milk begins to coagulate after two or three minutes. The tube is now cautiously heated with a small flame for about one minute, when the liquid butter fat neatly separates, and may be measured.

The fat may also be dissolved in ether and afterwards weighed.

L. DE K.

**Effect on Butter of Feeding with Sesame and Cotton Cakes.**

By V. STEIN (*Bied. Centr.*, 1895, 24, 93—94; from *Tidskr. f. Landökon.*, 1894, 13, 664).—Butter examined during prolonged feeding with sesame cake gave negative results when tested for Baudonin's (? Baudouin) and Becchi's reactions. The substance in sesame oil which shows Baudonin's reaction does not therefore pass into the milk even when an unusually large amount of sesame cake is given to cows. Similar experiments made with cotton cake shows that the substance which shows the Becchi reaction passes into the milk and butter. Whilst therefore a sesame oil reaction in butter would indicate adulteration with margarine containing sesame oil, Becchi's reaction would not necessarily prove the presence of margarine containing cotton-seed oil.

N. H. J. M.

**Urea in the Blood.** By CH. EUGÈNE QUINQUAUD (*Compt. rend. soc. Biol.*, 1893, 952—956).—Most previous methods for estimating the amount of urea in the blood involve the evaporation of alcoholic extracts of the blood in the water bath. This, however, leads to a partial decomposition of the urea, the loss being stated to be from 10 to 30 per cent. The temperature should not be raised above 35°, and concentration is best carried out in a vacuum; an apparatus, by means of which this can be easily accomplished, is described.

W. D. H.

**Solubility of Quinine in Alkalis.** By EMMANUEL DOUMER and E. DERAUX (*J. Pharm.*, 1895, [6], 1, 50—59).—The authors determined the solubility by gradually adding a 1 per cent. solution of sulphate of quinine to a known quantity of the alkali of known strength, and observing the point at which a permanent precipitate was formed. Detailed tables of the results are given.

*Ammonia.*—The actual amount of quinine dissolved by 100 c.c. of ammonia increased from 0.042 gram by a 0.26 per cent. solution to 0.092 by a 17.9 per cent. solution; but, reckoned per gram of ammonia, these results decrease from 0.163 gram for the weaker solutions to 0.006 gram for the stronger. For complete precipitation of the quinine, the smallest possible quantity of ammonia should therefore be employed.

*Soda.*—The quinine dissolved by 100 c.c. of soda ranged from 0.046 gram by a 0.0035 per cent. solution to 0.0075 gram by a 8.54 per cent. solution, or, per gram of soda, from 13.14 grams to 0.001 gram.

*Potash.*—The quinine dissolved by 100 c.c. of solution decreased from 0.044 gram by a 0.306 per cent. solution to 0.003 gram by a

22.3 per cent. solution, or from 0.144 to 0.0001 gram per gram of potash.

*Influence of Alkali Carbonates.*—The presence of an alkali carbonate in the alkaline solution greatly diminishes its solvent power for quinine, and it is possible that the numbers given for potash and soda are lower than they should be, owing to the presence of carbonate as an impurity. Ammonium carbonate largely increases the solvent power of potash and soda (probably owing to the formation of free ammonia), but decreases that of ammonia.

For complete precipitation of quinine by the fixed alkalis, a considerable quantity of alkali of high concentration should therefore be used, and it is advisable for the alkaline solution to contain carbonate.

L. T. T.

**Detection of Colchicine.** By ERNEST BARILLOT (*Bull. Soc. Chim.*, 1894, [3], 11, 514—516).—To detect colchicine, the suspected alkaloid in the form of the free base is heated with oxalic acid (0.25 gram) and concentrated sulphuric acid (1 c.c.) for an hour at 120°, and the product is diluted with water. If colchicine is present, the colour is yellow before the heating and reddish-brown afterwards, and is not affected by the dilution with water. Excess of alcoholic soda is now added, followed by excess of acetic acid, and the acid solution is extracted with chloroform; if colchicine were originally present, the chloroform extract would contain a yellow colouring matter, which, when dried, yields a violet-red coloration with concentrated nitric acid, and a raspberry-red with concentrated sulphuric acid. If the colouring matter is not entirely taken up by the chloroform, but floats about in flakes, it may be collected on a very small filter, and the dried strips of the latter immersed in the acids.

Ptomaines give no reaction under this treatment. Morphine and codeine also yield coloured products, but these are quite distinct. The test is practicable even with  $\frac{1}{6}$  milligram of colchicine.

JN. W.

**Fibrinolysis.** By A. DASTRE (*Compt. rend. soc. Biol.*, 1893, 995—997).—In estimating fibrin in blood or similar liquids, it is necessary to observe four conditions: (1) to agitate the blood with some substance like ebonite, particles of which do not become entangled with the clot; (2) to wash the magma under a current of water, but without kneading, for 24 hours; (3) to weigh the fibrin in the dry state after an exposure to a temperature of 105° for 48 hours; and (4) not to allow the fibrin, after its deposition, to remain in contact with the liquid from which it originated. This last condition is necessitated by the fact here designated fibrinolysis: that is, fibrin left in contact with the blood slowly disappears; the average of about 15 experiments shows a loss of about 8 per cent. of fibrin in 18 hours.

W. D. H.

**Densimetric Estimation of Albumin.** By THEODOR LOHNSTEIN (*Pflüger's Archiv*, 1895, 60, 136—138; compare this vol., ii, 191).—Further details are given, which have for their object the shortening of the operations previously described, so that an estimation may be made in half an hour.

W. D. H.



## General and Physical Chemistry.

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**Dissociation and the Optical Rotation of Active Compounds.** By EBERHARD RIMBACH (*Zeit. physikal. Chem.*, 1895, **16**, 671—676).—If the increase of the optical rotation of an active compound consequent on dilution is due to dissociation, the degree of dissociation should be given by the formulæ  $n = 100 \frac{[\alpha] - [\alpha]_0}{[\alpha]_\infty - [\alpha]_0}$ , where  $[\alpha]$  is the rotation of the solution examined,  $[\alpha]_0$  and  $[\alpha]_\infty$  that at infinite concentration and dilution respectively. The salt selected for examination was rubidium tartrate, and 10 determinations of the rotation were made, the concentration varying from 64.49 per cent. to 1.57 per cent. of the solution. From the results, by an extrapolation formula, the values  $[\alpha]_\infty = 19.51$  and  $[\alpha]_0 = 25.63$  were obtained. The degree of dissociation thus obtained, as compared with that found from the conductivity, gave the following results.

Per cent. of salt. . . . .	29.84	20.26	10.25	5.11	1.57
Electrolytic. . . . .	39.4	46.9	56.0	62.4	72.9
Optical. . . . .	53.5	69.2	83.8	92.4	97.7

The author considers that the divergence between the two methods is probably owing to a specific influence of the solvent at high concentrations; for example, in the formation of hydrates, decomposition of molecular complexes, &c. Experiments were also performed with light of other wave-lengths, namely, red,  $\lambda = 661$ ; green,  $\lambda = 533$ ; blue,  $\lambda = 489$  and  $\lambda = 448$ ; but the values for the dissociation are all closely concordant, so that the nature of the light appears immaterial.

L. M. J.

**Relation between Electrolytic Dissociation and Optical Rotation.** By GIACOMO CARRARA and G. GENNARI (*Gazzetta*, 1894, **24**, ii, 484—491; compare Carrara, *Abstr.*, 1894, ii, 178, and Hädrich, *Abstr.*, 1894, ii, 73).—A study of the optical activity of aqueous solutions of amyl hydrogen sulphate and its salts, and of diisoamylamine and its salts, shows that in fairly dilute solutions the molecular rotation of the salts is practically the same as that of the active base or salt contained in them; this is in agreement with the electrolytic dissociation hypothesis, the salts of strong acids and bases such as those used being highly dissociated in solutions of the concentrations employed.

Amyl hydrogen sulphate and its potassium, sodium, and ammonium salts, and diisoamylamine and its sulphate, acetate, and propionate were examined; cryoscopic determinations showed that the three metallic salts are highly dissociated in aqueous solutions of the concentrations used.

The slight differences between the observed molecular rotations is accounted for by the incomplete dissociation of the salts. No refer-

ence is made to the recent work of Walden (this vol., ii. 65) on the same subject. W. J. P.

**Electrolytic Dissociation and the Law of Dilution in Organic Solvents.** By GIACOMO CARRARA (*Gazzetta*, 1894, 24, ii, 504—535).—In a previous paper (Abstr., 1894, ii, 310), the author has shown that the velocity of formation of triethylsulphine iodide from ethylic iodide and sulphide is considerably affected by the addition of various neutral solvents; with the object of ascertaining whether these alterations in the speed of the action are due to electrolytic dissociation set up by the solvent, determinations of the electrical conductivity of triethylsulphine iodide have been made in water, methylic, ethylic, propylic, isopropylic, primary and tertiary isobutylic, isoamyllic, allylic, and benzylic alcohols and acetone. The electrical conductivity of very dilute acetone and methylic alcohol solutions is greater than that of the aqueous solutions, whilst in concentrated solutions the reverse is the case; not only then is water not the only solvent which induces electrolytic dissociation, but other solvents may act even more strongly than water in this respect. Piccini has recently investigated the very similar behaviour of chromic chloride dissolved in water and in methylic alcohol (this vol., ii, 229). In the cases of the saturated aliphatic alcohols, the dissociating powers of the various neutral solvents employed are of the same orders as the velocities of reaction between ethylic iodide and sulphide and as Menshutkin's values for the speeds of formation of tetrethylammonium iodide; considerable disproportionality is, however, noted when allylic or benzylic alcohol or acetone is employed as the neutral solvent; the purely qualitative nature of the agreement is probably due to the fact that the conductivities and speeds of reaction were measured at very different temperatures. On the ground of the determinations of the dissociation constants of triethylsulphine iodide in acetone and the various alcohols, the author concludes that the law of dilution holds in these organic solutions, and thus combats the conclusions of previous workers on this subject.

The extent to which electrolytic dissociation occurs in the organic solvents named above is found to be much smaller by the Beckmann method than by the electrical conductivity method; the discrepancy between the two methods is attributed to the existence of molecular complexes of the salt in solution as well as of chemical molecules and ions (compare Wildermann, Abstr., 1894, ii, 227).

The author examines qualitative similarities in order of magnitude between the dissociation constants, the dielectrical constants, and the coefficients of internal friction of the solvents employed in the present investigation and the molecular conductivities of dilute solutions of triethylsulphine iodide in them. W. J. P.

**Thermochemical Carbon Battery.** By DÉSIKÉ KORDA (*Compt. rend.*, 1895, 120, 615—618).—Experiments made with a view to ascertain whether in the reduction of metallic oxides there is a development of electrical energy, show that only in two of the cases investigated is there any distinct electromotive force. Barium per-

oxide in contact with carbon heated at dull redness gives an E.M.F. of about 1 volt. Other peroxides, such as those of manganese and lead, show no similar behaviour, probably because the product of reduction is a conductor and forms short circuits with the carbon. Copper peroxide and carbon, when separated by fused potassium carbonate, give an E.M.F. of 0.9 to 1.1 volt. If the potassium carbonate contains water, the current is at first in the opposite direction, but changes as the temperature rises.

In both cases, the E.M.F. is considerably lower than that calculated from the known thermal disturbances, and it follows that only part of the energy is liberated as electrical energy. Faraday's law is not applicable, because of the continuous supply of extraneous energy in the form of heat.

C. H. B.

**Electrocapillary Phenomena.** By H. LUGGIN (*Zeit. physikal. Chem.*, 1895, **16**, 677—707).—If mercury or an amalgam be made the cathode for the polarisation of an aqueous solution, the capillary constant increases with the E.M.F. until it reaches a maximum value, when the E.M.F. is equal to the potential difference between the metal and liquid; beyond this point, it decreases. Experiments were made in which the solution was replaced by a molten salt, namely, (i) a mixture of lithium and potassium bromides, (ii) sodium and lithium chlorides, (iii) zinc chloride, and (iv) potassium and sodium nitrates. For the two latter cases, curves are given with the capillary constant as ordinate and the potential difference as abscissa. In the case of the zinc chloride, no maximum is obtained, whilst it occurs in the case of the nitrates at 0.69 volt below the natural potential of the mercury. A number of observations are also recorded for aqueous solutions at equivalent concentrations. The first series of experiments was on alkalis and acids; for the former, the mean value for the maximum was -0.859 volt (0.915 to 0.835), for the latter the values varied from -0.922 to -0.849 volt, with a mean of -0.882. In the case of halogen salts and organic acids, the values vary within considerable limits, especially for the former. Here, therefore, the potential is not independent of the nature of the solution. The influence of the metal is next considered, experiments being made with mercury and with Lipowitz's alloy. The curves are not coincident, the alloy having its highest capillary constant at the natural potential and about 0.3 volt below that of the mercury. The author then discusses the bearing of these results on Helmholtz's theory, with which he considers they are not in accord, and which he regards as an unsatisfactory explanation.

L. M. J.

**New Fractionating Column.** By ERNEST BARILLOT (*Bull. Soc. Chim.*, 1894, [3], **11**, 929—931).—A modification of the Le Bel-Henninger column. The vapour, after leaving the flask by the usual exit tube, and before entering the condenser, passes through a series of bulbs, in which it is washed, at any desired temperature, by the liquid resulting from the condensation of its less volatile constituents. The temperature is regulated by means of a suitable bath, and the overflow from the bulbs carried back to the main column by special tubes

entering the latter at the junctions of the main bulbs. Trials with mixtures of methylic alcohol and acetone are stated to have yielded good results. JN. W.

**Comparative Investigation of the Methods of Fractional Distillation.** By F. ANDERLINI and R. SALVADORI (*Gazzetta*, 1895, 25, i, 1—31).—A large number of experiments with various forms of the fractionating columns of Wurtz, Linnemann, Glinsky, Hempel, Le Bel, Henninger, and Anderlini have been made with mixtures of alcohol and water, of benzene, toluene, and xylene, and of aniline and xylidine, in order to determine which pattern of column gives the most satisfactory results. A spiral form of fractionating column such as that devised by Anderlini (*Abstr.*, 1894, ii, 329) seems to be one of the best, whilst the other types of column in use differ but slightly in efficiency under particular conditions. W. J. P.

**Dephlegmator for Fractional Distillation.** By SYDNEY YOUNG and G. L. THOMAS (*Chem. News*, 1895, 71, 177).—In the tube constituting the still-head, sharp constrictions are formed, at intervals of about 8 cm., and upon these rest discs of platinum gauze, through the centre of which pass hook-shaped short tubes open at both ends; the straight shaft of the hook extends slightly above the gauze, and is of larger bore than the hook, which is pendant below the gauze. D. A. L.

**The Critical Temperature as a Criterion of Chemical Purity.** By RUDOLF KNIETSCH (*Zeit. physikal. Chem.*, 1895, 16, 731—732).—The author had in 1890 pointed out that the critical temperature forms a good criterion of the chemical purity of a compound; he considers therefore that the priority for this belongs to himself, not to Pictet and Altschul (*this vol.*, ii, 200). L. M. J.

**Thermal Constants of Calcium Oxybromide and Oxyiodide.** By TASSILLY (*Bull. Soc. Chim.*, 1894, [3], 11, 931—933).—*Calcium oxybromide*,  $\text{CaBr}_2 \cdot 3\text{CaO} \cdot 16\text{H}_2\text{O}$ , prepared by adding lime (3 grams) in small portions to a warm solution of bromine (100 grams) in water (75 c.c.), crystallises in nacreous spangles composed of minute needles. The corresponding oxyiodide (*Abstr.*, 1894, ii, 92) may be advantageously prepared in a similar manner. The oxy-salts are much less hygroscopic than the corresponding haloids; they are soluble in dilute hydrochloric and nitric acids, but are decomposed by water and alcohol.

The heat of dissolution of the oxybromide in dilute hydrobromic acid is 63.55 Cal., and the heat of formation of the solid substance from its solid constituents is 76.45 Cal. The heat of dissolution of the oxyiodide in dilute hydriodic acid is 63.30 Cal., and the heat of formation of the solid substance from its solid constituents is 79.90 Cal. It is noteworthy that the heat of dissolution of the oxychloride in dilute hydrochloric acid is 63.12 Cal., so that the heats of dissolution of the three salts in the corresponding halogen acids are practically identical. JN. W.

**Heat of Formation of Mercuric Salts.** By RAOUL VARET (*Compt. rend.*, 1895, 120, 620—622).—The heat of formation of mercuric iodide was determined by dissolving the metal in a solution of iodine in potassium iodide. The heats of dilution of this solution, and the heats of dissolution of iodine and of mercuric iodide in potassium iodide solution, being also measured.

$\text{Hg liq.} + \text{I}_2 \text{ sol.} = \text{HgI}_2 \text{ cryst. red.} \dots \text{ develops } +24.7 \text{ Cal.}$

Direct determination of the heat of formation of mercuric bromide gave

$\text{Hg liq.} + \text{Br}_2 \text{ liq.} = \text{HgBr}_2 \text{ sol.} \dots \text{ develops } +40.7 \text{ Cal.}$

which agrees with Nernst's value (40.5 Cal.).

From these results and Berthelot's earlier observations on the action of dilute hydracids on mercuric oxide, it follows that

$\text{Hg liq.} + \text{O gas} = \text{HgO sol.} \dots \text{ develops } +21.3 \text{ Cal.}$

$\text{Hg liq.} + \text{Cl}_2 \text{ gas} = \text{HgCl}_2 \text{ sol.} \dots \text{ ,, } +49.8 \text{ ,,}$

C. H. B.

**Isomeric Mercuric Oxides.** By RAOUL VARET (*Compt. rend.*, 1895, 120, 622—623).—Red mercuric oxide obtained by the action of heat on the nitrate was dissolved in dilute hydrocyanic acid at  $12^\circ$ .

$\text{HgO red} + 2\text{HCN dil.} = \text{Hg(CN)}_2 \text{ diss.}$

$+ \text{H}_2\text{O liq.} \dots \text{ develops } +31.55 \text{ Cal.}$

Berthelot found that under the same conditions and at the same temperature, yellow mercuric oxide develops +31.60 Cal. It follows that the conversion of the yellow into the red variety, or *vice versa*, is accompanied by no thermal disturbance, a result which explains why both forms are equally stable at the ordinary temperature, unlike the yellow and red iodides.

C. H. B.

**Heats of Formation of some Iron Compounds.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1895, 120, 623—625).—The substance under investigation was mixed with carbon and burnt in oxygen in the calorimetric bomb. Under these conditions, the heat of combustion of the substance is ascertained from the difference between the rise of temperature observed when the substance is present and when the same weight of carbon is burnt alone. The oxides of iron are converted into the oxide  $\text{Fe}_3\text{O}_4$ , the heat of formation of which is  $4 \times 67.2 \text{ Cal.}$  Experiments were made with the two varieties of ferric oxide, one obtained by heating ferric nitrate at  $400^\circ$ , the other by heating the first product at  $1000^\circ$ . The results obtained are as follows.

$\text{FeO} + \frac{1}{3}\text{O} = \frac{1}{3}\text{Fe}_3\text{O}_4 \dots \text{ develops } +25.2 \text{ Cal.}$

$\text{Fe} + \text{O} = \text{FeO} \dots \text{ ,, } +64.6 \text{ ,,}$

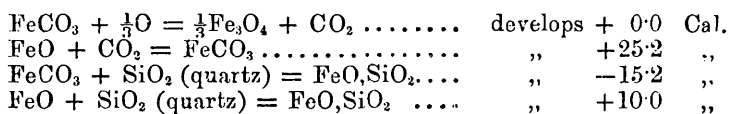
$\text{Fe}_2\text{O}_3 \text{ ordinary} = \text{Fe}_2\text{O}_3 \text{ calcined} \dots \text{ ,, } +2.14 \text{ ,,}$

$\text{Fe}_2\text{O}_3 \text{ calcined} = \frac{2}{3}\text{Fe}_3\text{O}_4 + \frac{1}{3}\text{O} \dots \text{ ,, } -15.06 \text{ ,,}$

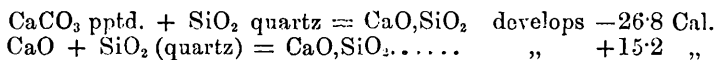
$2\text{Fe} + \text{O}_3 = \text{Fe}_2\text{O}_3 \text{ calc.} \dots \text{ ,, } +3 \times 64.8 \text{ ,,}$

$2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3 \text{ calc.} \dots \text{ ,, } +65.2 \text{ ,,}$

The combination of oxygen with ferrous oxide develops practically the same quantity of heat as its combination with iron.



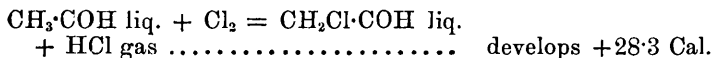
With calcium carbonate and silica, the results are of the same order as with ferrous carbonate, as regards the difference between the heats of formation of carbonate and silicate.



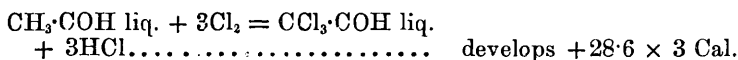
Comparison of the results obtained by the bomb method with those obtained in solutions indicate that the former is capable of considerable accuracy.

C. H. B.

**Chloraldehydes.** By PAUL RIVALS (*Compt. rend.*, 1895, **120**, 625—627).—The heat of combustion of chloraldehyde is +233.5 Cal., the heat of formation from its elements is +63.4 Cal., and hence

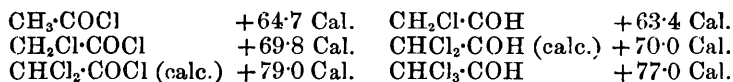


Taking Berthelot's value for the heat of formation of chloral from its elements (+77.0 Cal.), it follows that



It would seem that the thermal disturbances accompanying successive substitutions of chlorine in aldehyde increase more regularly than in the case of acetic acid. The heat of formation of liquid dichloraldehyde from its elements is probably about +70 Cal.

The following table shows that the heats of formation of the chloraldehydes from their elements are practically identical with those of the corresponding chloracetic chlorides.



Regarding an acid chloride as derived from an aldehyde by the substitution of chlorine for hydrogen in the aldehydic group, it follows that the conversion of  $\text{CH}_3\cdot\text{COH}$  into  $\text{CH}_3\cdot\text{COC l}$  develops +29.6 Cal.,  $\text{CH}_2\text{Cl}\cdot\text{COH}$  into  $\text{CH}_2\text{Cl}\cdot\text{COC l}$ , +28.4 Cal., and  $\text{CCl}_3\cdot\text{COH}$  into  $\text{CCl}_3\cdot\text{COC l}$ , +38.2 Cal. The last term obviously differs considerably from the others, and a similar difference has been observed by Berthelot and Longuiné in the heats of oxidation of the aldehydes to acids.  $\text{CH}_3\cdot\text{COH}$  into  $\text{CH}_3\text{COOH}$  develops +62.6 Cal., and  $\text{CH}_2\text{Cl}\cdot\text{COH}$  into  $\text{CH}_2\text{Cl}\cdot\text{COOH}$ , +62.5 Cal., but  $\text{CCl}_3\cdot\text{COH}$  into  $\text{CCl}_3\cdot\text{COOH}$  develops +67.7 Cal.

C. H. B.

**Crystallised Polymeride of Chloraldehyde.** By PAUL RIVALS (*Compt. rend.*, 1895, 120, 627—628).—The heat of combustion of the crystallised polymeride of chloraldehyde ( $C_2H_3ClO$ )<sub>n</sub> is (+229·3 Cal.)<sub>n</sub>, and its heat of formation from its elements (+67·7 Cal.)<sub>n</sub>, and hence the formation of the polymeride is accompanied by a development of +4·4 Cal. for each molecule of the chloraldehyde. It would seem therefore that this polymeride is analogous to metaldehyde and not to paraldehyde. The analogy is also seen in the fact that, like metaldehyde, it is only slightly soluble in water. C. H. B.

**Relation between the Molecular Weight and Density of Liquid and Solid Substances.** By UGO ALVISI (*Gazzetta*, 1895, 25, i, 31—41).—The equivalent weight of a liquid or solid substance divided by its density gives a constant to which the term equivalent volume is given. The author has investigated the equivalent volumes of several series of salts, and finds that substances belonging to the same class have approximately the same equivalent volume; thus the chlorides, including chlorine and hydrogen chloride, have equivalent volumes of about 26, the bromides have a common equivalent volume of about 32, whilst for the iodides the value is about 38; very considerable variations from these numbers, however, occur, the highest values being obtained in the case of those salts, such as mercurous chloride and thallous chloride, the metals of which are capable of combining with a larger proportion of halogen; ferric and chromic chlorides have equivalent volumes much below the average. The equivalent volumes of the fluorides are about one-half of those of the corresponding chlorides. W. J. P.

**Volumes of Aqueous Salt Solution between 100° and 150°.** By K. ZEPERNICK and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1895, 16, 659—670; compare Abstracts, 1894, ii, 224, 268, 342, 410; this vol., ii, 204).—As the isobars for quantities of water which have the same volume at 0° again cut at about 120° or 130°, it appeared probable that if solutions at different concentrations possessing equal volumes at 0° were examined, they would be found to again have equal volumes at about this temperature; at least in those cases where  $\Delta k$  is independent of the temperature. The volume relations were therefore determined in the case of solutions of sodium, potassium, calcium, and hydrogen chlorides, sodium hydroxide, and sodium sulphate. Dilatometers furnished with an auxiliary bulb were employed, and the volumes taken directly at temperatures between 100° and 150°; corrections due to compressibility of the glass and solution have to be employed. The values so obtained for water are compared with, and are in all cases smaller than, those obtained by Hirn. Interpolation formulæ for the volume are obtained and the curves found to cut those of pure water at the following temperatures.

Sodium chloride .....	130°	164°	137°
Potassium chloride .....	126	127	121
Hydrogen chloride .....	116		

Hydrogen sulphate....	151°	151°		
Sodium hydroxide ....	127	129		
Sodium sulphate.....	144	138		
Sodium carbonate.....	131	143		
Calcium chloride.....	118	110	105°	96°

With the exception of those of calcium chloride, therefore, the isobars all cut that of water in the manner predicted. L. M. J.

**Cause of Osmotic Pressure and Ionisation (Electrolytic Dissociation).** By ISIDOR TRAUBE (*Zeit. anorg. Chem.*, 1895, **8**, 323—337).—The author shows that the equivalent of any ion exercises always the same attraction for the water, and that this attraction is equal to that exercised by the molecule of any non-dissociated substance, the contraction caused by this attraction being for the gram-equivalent or molecule 12.2 c.c. (compare this vol., ii, 209). As equivalent quantities of different ions have all the same attraction for the solvent, their osmotic pressures must be the same. Therefore laws analogous to those of Boyle, Gay-Lussac, and Avogadro must hold for the osmotic pressure. When the electrolyte is dissolved in water, the same attraction that may be looked on as the cause of osmotic pressure also causes the weakening of the hold of the ions on one another. The law that equivalent amounts of the different ions produce, on being dissolved in water, the same contraction in volume, may be compared to Faraday's law that equivalent amounts of the different ions require for their separation the same quantity of electricity. Drude and Nernst regard the electrical charging of the ions as the cause of the volume contraction (*Zeit. physikal. Chem.*, **15**, 79). The analogy between the volume law and Faraday's law is, however, rather proof that the ions in solution are not electrically charged and only become so at the moment of their separation, the charging of the ions being the consequence and not the cause of the volume contraction, space energy being thus converted into electrical energy. H. C.

**Molecular Weight Determinations of Solid, Liquid, and Dissolved Substances.** By ISIDOR TRAUBE (*Zeit. anorg. Chem.*, 1895, **8**, 338—347).—The method proposed is that described in a former paper (see this vol., ii, 209). In cases in which association of the molecules to complexes occurs, the factor of association  $x = 12.2/(V_m - v_m)$ . Calculations of  $x$  for a large number of different compounds are given. In homologous series,  $x$  decreases with rising molecular weight, the decrease being most marked in the lower terms. Isomeric compounds often have different values of  $x$ . The hydroxyl group causes the greatest increase in  $x$ , but in this case also a decrease takes place with rising molecular weight. H. C.

**Solubility in Mixtures of Alcohol and Water.** By GUIDO BODLÄNDER (*Zeit. physikal. Chem.*, 1895, **16**, 729—730).—The author had previously shown that the solubility, in mixtures of alcohol and water, of substances soluble in the latter but insoluble in the former may in some cases be expressed by the expression  $W/\sqrt[3]{S} = \text{constant}$ ,



where W and S are the percentages of water and of the compound. The expression is now again tested for the compounds trinitrobenzene, benzamide, and alanine. In the case of benzamide, the expression is inapplicable, this compound being soluble in alcohol. For the other two the constancy of the expression is fairly satisfactory, especially in the case of alanine. The solubilities are taken from the experiments of Holleman and Antusch.

L. M. J.

**Isomorphism, XI.** By JAN. W. RETGERS (*Zeit. physikal. Chem.*, 1895, **16**, 577—658; see also this vol., ii, 160).—The first portion of the paper deals further with the question of the chemical union of isomorphous salts and contains the results of the author's researches on mixed crystals of the salts of nickel and iron, iron and manganese, and copper and manganese, whilst a table of the literature dealing with the crystallography of the vitriols is also added.

The question of the isomorphism of cadmium with the metals of the zinc series is considered. Cadmium sulphate may be represented as  $\text{CdSO}_4 + 3\text{H}_2\text{O}$ , although the recorded analyses do not completely agree with this water content. The mixed crystals of this salt with the sulphates of iron and copper were examined, and owing to the existence of an extended series of mixed crystals with the former, the author considers that cadmium must be undoubtedly placed in the magnesium series.

A series of compounds of isomorphous elements are next considered, namely (1) compounds of the halogens such as  $\text{ICl}_3$ , &c., (2) double haloid salts of metals and nonmetals such as  $\text{SnBr}_2\text{Cl}_2$ , &c., (3) compounds such as  $\text{KI}_2$ , which may, however, be regarded as pure additive products. With respect to the second class, the author considers that the evidence that they are really compounds and not mixtures is insufficient, whilst in the first class he points out that isomorphism of compounds does not necessitate isomorphism of the free elements.

I.	II.	III.	IV.	V.	VI.	VII.
H	Li	Be	B	C	N	O
Fl	Na	Mg	Al	Si	P	S
Cl	K	Ca	Sc	Ti	V	Cr, Mn, Fe, Co, Ni
—	Cu	Zn	Ga	Ge	As	Se
Br	Rb	Sr	Y	Zr	Nb	Mo, Ru, Rh, Pd
—	Ag	Cd	In	Sn	Sb	Te
I	Cs	Ba	La, Ce, Di, Sm, Er, Yb	—	Ta	W, Os, Ir, Pt
—	Au, Hg, Tl	Pb	—	—	Bi	Th, U

The supposed compounds of sulphur and selenium are regarded as mixtures only, the same holding for the double chromates and sulphates.

The next portion of the paper deals with the value of the etched-figures upon crystals in the problems of isomorphism. Many cases are indicated where the study of such figures, caused by various etching media, would be most useful in doubtful cases of isomorphism, and the author considers a very fruitful field of research to lie in this direction.

The table usually employed to illustrate the periodic law is next considered, and its chief defects pointed out, namely, (1) the position of hydrogen is uncertain, (2) the gaps are probably too numerous, and (3) the indication of isomorphism is unsatisfactory, whilst (4) many metals fall into their wrong position. A table (p. 309) is therefore given in which the author considers these objections are overcome. The first two columns may be united in one.

The paper concludes with a note on the law of the relation between chemical simplicity and crystalline form, which the author considers must, as pointed out by van't Hoff, be ascribed to Buys Ballot.

L. M. J.

**Affinity Constants of Dibasic Acids and of Acid Ethereal Salts.** By RUDOLF WEGSCHEIDER (*Monatsh.*, 1895, **16**, 153—158).—The author shows that in a dilute solution of a dibasic acid, the numbers of the isomeric ions which are formed are proportional to the affinity constants of the two carboxylic groups,  $K_1$  and  $K_2$ ; and further that the constant of affinity of a dibasic acid is equal to the sum of the affinity constants of the two carboxylic groups,  $K = K_1 + K_2$ . If the acid is symmetrical, then the constants for the two carboxyls are identical, and the constant for the acid becomes double that for one of the carboxyls  $K = 2K_1$ . In unsymmetrical acids, the relationship of the constants for the two carboxyls is more complex. This relationship in the case of hemipinic acid may be obtained from the constants of the two isomeric monomethylic salts,  $K_\alpha$  and  $K_\beta$ .

$$K_\alpha = a \cdot K_1 \text{ and } K_\beta = a \cdot K_2 \quad \therefore \frac{K_1}{K_2} = \frac{K_\alpha}{K_\beta} = \frac{1}{8}.$$

It is further shown that the following rules are approximately true. (1) The affinity constant of a symmetrical dibasic acid is double that of its mono-methylic or mono-ethylic salt. (2) The affinity constant of an unsymmetrical dibasic acid is equal to the sum of the constants for the two isomeric mono-alkylic salts.

J. J. S.

**Affinity Constants of Ureides and Isonitroso-derivatives.** By P. A. TRÜBSBACH (*Zeit. physikal. Chem.*, 1895, **16**, 708—728).—The paper contains the results of the determinations of the conductivity of a large number of carbamide derivatives. For carbamide itself, thiocarbamide, methylene carbamide, ethylene carbamide, and hydantoin, the conductivities were all small; the highest value ( $v = 256$ ) being 0.4. Parabanic acid, measured 20 minutes after

solution, gave the value  $\mu_{1624} = 10.8$ , but finally reached an end value of  $\mu_{1024} = 242.3$ . This, and the end value of oxaluric acid, agreeing with the conductivity of carbamide oxalate at a similar dilution, indicates the hydrolysis of these two compounds and formation of the latter. Methylparabanic acid is, in a similar manner, shown to form methylcarbamide oxalate.

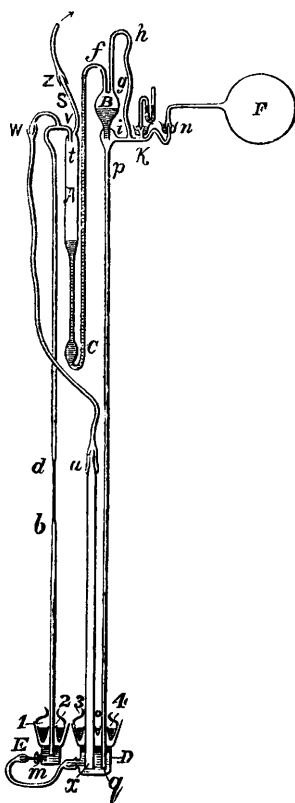
Thioparabanic acid gave  $\mu_{1024} = 5.7$ , but, later,  $\mu_{1024} = 3.2$ , a change which the author considers is due to the molecular change from  $\text{CS} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$  to  $\text{NH} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{S} - \text{CO} \end{smallmatrix}$ . A large number of derivatives of barbituric acid were next examined, the acid itself being found to form normal salts with only 1 molecule of a base. Alloxan, and a number of uracil derivatives are also examined, and a few isonitroso-compounds.

Of these, acetoxime is very feebly dissociated, being practically a non-electrolyte, the same obtaining to a less extent for phenylmethylketoxime. Quinoxime shows indications of decomposition in the decrease of the affinity constant. In the case of the naphthol derivatives,  $\alpha$ -nitroso- $\beta$ -naphthol and  $\beta$ -nitroso- $\alpha$ -naphthol give identical results, both differing from, and smaller than, the values for  $\alpha$ -nitroso- $\alpha$ -naphthol.

L. M. J.

**Automatic Vacuum-pump.** By M. I. PUPIN (*Amer. J. Sci.*, 1895, [3], 49, 19—21).—A suction-pump and an ordinary Sprengel pump *Bq* are connected together by a syphon barometer *Cf*. The reservoir *A* is connected with a water or other suction-pump which draws the mercury from the vessels *E* and *D* up the tubes *mv*, *ux*, and when these vessels are emptied to the level of the lower end of the tube *mv*, the column of mercury in the latter tube (*mv*) is forced by the external air into *A*, whence it passes through the syphon *Cf* into the upper reservoir *B* of the Sprengel pump, and in descending again into *D* the vessel *F* is exhausted.

L. J. S.



## Inorganic Chemistry.

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### Action of Nitrous Oxide on Metals and Metallic Oxides.

By PAUL SABATIER and J. B. SENDERENS (*Compt. rend.*, 1895, **120**, 618—620).—The authors have made, with nitrous oxide, observations similar to those already recorded in the case of nitric oxide and nitric peroxide (Abstr., 1892, 1151, 1271, 1390; and 1894, ii, 90). Cadmium, at about  $320^{\circ}$ , volatilises and oxidises at the same time, yielding a brown sublimate of the oxide. Finely-divided lead, obtained by reduction, oxidises slowly at about  $300^{\circ}$ , and yields yellow lead oxide. Reduced iron burns below  $170^{\circ}$  with formation of ferric oxide. Reduced cobalt burns incompletely at about  $230^{\circ}$ , and yields the brown monoxide. Reduced nickel oxidises with incandescence at  $300^{\circ}$ , and yields the monoxide. Reduced copper remains unaltered at  $200^{\circ}$ , but above  $250^{\circ}$  it is slowly transformed into red cuprous oxide; at a dull red heat there is some incandescence, but the product is the same.

Manganous oxide oxidises with incandescence at about  $350^{\circ}$ , and yields the pale brown oxide,  $Mn_3O_4$ . Tungsten dioxide, at about  $450^{\circ}$ , is converted, without incandescence, into the oxide  $W_2O_6$  without any admixture of tungstic anhydride. Black molybdenum trioxide,  $Mo_2O_3$ , slowly changes into the violet oxide,  $MoO_2$ . Stannous oxide burns at about  $400^{\circ}$ , and yields stannic oxide. Cuprous oxide does not alter at  $350^{\circ}$ . Vanadium trioxide also is not affected below  $500^{\circ}$ . Uranous oxide, obtained by reducing uranic oxide in hydrogen at a bright red heat, is not affected by nitrous oxide at  $450^{\circ}$ , but if reduced at a lower temperature it burns in the nitrous oxide at about  $400^{\circ}$ , and yields the black oxide,  $U_2O_5$ .

Below  $500^{\circ}$ , the products of oxidation by nitrous oxide differ but little from those obtained from nitric oxide. Incandescence is only produced at a higher temperature, and is always less brilliant with nitrous than with nitric oxide.

Except in the case of iron, nitric oxide is a slightly more powerful oxidising agent than nitrous oxide. In both cases oxidation is due to the direct action of the gas, and cannot be attributed to its preliminary decomposition with liberation of oxygen; if this were the case, cuprous oxide would be oxidised.

When nitrous oxide is passed into sodium peroxide fused at about  $300^{\circ}$ , sodium nitrite is formed, and nitrogen is liberated, as Vernon Harcourt has previously observed. A similar result is obtained with barium peroxide below a red heat. Lead peroxide, on the other hand, splits up into lead monoxide and oxygen, whereas, with nitric oxide, it yields nitric peroxide and basic lead nitrate.

C. H. B.

**Action of Heat on Carbon Bisulphide.** By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1895, **8**, 314—317).—The author has examined the decomposition which takes place when carbon bisulphide is slowly distilled through a glass tube heated at  $600^{\circ}$ . The product, after 15

distillations, was subjected to fractional distillation. Two hundred and fifty c.c. came over at  $46.2^{\circ}$  under 752 mm. pressure; the residue, which was olive-green, was more viscid than carbon bisulphide, and yielded, on distillation, 20 c.c. at  $46.5^{\circ}$ , 16 c.c. at  $47.1^{\circ}$ , 8 c.c. at  $48.5^{\circ}$ , and a residue of 5 c.c., which consisted of an oily, red liquid, having a very evil odour; finally, there remained in the distillation flask a small quantity of brownish-red oil, which did not distil. This red oil the author believes to be the carbon sesquisulphide, described by v. Lengyel (Abstr., 1894, ii, 90). When heated on a watch-glass at  $120^{\circ}$ , it is converted into a black mass; when dissolved in chloroform and treated with bromine, a bright yellow precipitate is obtained: when allowed to remain exposed to air, it is converted into the black modification; this dissolves slowly in a solution of potassium hydroxide, and the red solution, when neutralised with hydrochloric acid, gives a precipitate of brown flocks.

The combustion tube through which the carbon bisulphide is distilled, becomes covered with a light black, lustrous mirror, which is not, however, due to the deposition of carbon, as it contains sulphur.

E. C. R.

**New Element from Bauxite.** By R. S. BAYER (*Bull. Soc. Chim.*, 1894, [3], 11, 1155—1162).—In preparing alumina on the manufacturing scale, red bauxite from Var is fused or boiled with caustic or carbonated alkali, and the alumina precipitated by carbonic anhydride from the alkali aluminate thus obtained. The residues contain the new element, in addition to iron, molybdenum, vanadium, and many others. The amount is a mere trace, as the whole product from 1,000,000 kilos. of bauxite weighed only 2 grams. On this account, no stoichiometrical determinations have yet been made, but the author hopes to furnish data later on.

It is unnecessary to enter into the details of the separation of the other elements, with the exception that the last to be eliminated were vanadium and molybdenum, with which the new element appears to be carried down by hydrogen sulphide from acid solutions, although it is not so precipitated when pure.

The element appears to exist in two states of oxidation, in the higher of which it forms a well-marked acid, which is probably allied to phosphoric and vanadic acids. The lower oxide is decidedly basic, although it appears to act under certain conditions as a feeble acid. Its compounds are, however, very unstable, and easily re-oxidised to those of the higher oxide.

The chlorides appear to be volatile, and afford well-defined spectra, having characteristic lines in the green, blue, and violet.

The *acid* is soluble in water, from which it is deposited, on evaporation, as a crystalline, yellow precipitate, fusing with difficulty at a bright red heat to a brownish-yellow mass. The *ammonium* salt crystallises from water in olive-green cubes, and is insoluble in concentrated ammonia. The *barium* salt is greenish-yellow, and insoluble in water, but soluble in acids; the *mercurous* salt forms straw-yellow, twinned crystals, and is insoluble in water, but soluble in nitric acid; the *silver* salt forms green crystals, and is soluble in nitric acid and ammonia; the *magnesium* salt is formed, in the presence of ammonium

chloride and ammonia, as a crystalline precipitate similar to magnesium ammonium phosphate. The acid resembles vanadic and phosphoric acids in forming a yellowish-white precipitate with nitromolybdic acid, but does not appear to react with hydrogen peroxide.

With alkali sulphides, it forms an intensely red solution, probably containing a *thio-acid*, as a sparingly soluble rust-coloured *sulphide* is precipitated from the solution by acids.

The acid is reduced by hydrogen sulphide in acid solution to the salt of a *lower oxide*, from which, after the hydrogen sulphide has been expelled in an atmosphere free from oxygen, alkalis precipitate a voluminous, dark, purple-brown *hydroxide*; this rapidly becomes crystalline, and is completely soluble in caustic alkalis, and partially in ammonia, yielding dark violet solutions, in which barium, strontium, and calcium chlorides produce violet precipitates.

JN. W.

**Atomic Weight of Strontium.** By THEODORE W. RICHARDS (*Zeit. anorg. Chem.*, 1895, 8, 253—273).—The author gives a critical account of the previous determinations of the atomic weight of strontium. The methods employed in the present investigation are the determinations of the ratio of silver to strontium bromide and of the ratio of silver bromide to strontium bromide.

Strontium bromide is very similar to the corresponding barium salt. It crystallises with  $6\text{H}_2\text{O}$ , is very hygroscopic, and melts in its water of crystallisation at  $100^\circ$ ; if allowed to remain in a desiccator for some time, it loses  $5\text{H}_2\text{O}$ . When heated in the air, it evolves a small quantity of bromine, but it can be dried in a current of dry hydrogen bromide, and the product thus obtained is neutral to phenolphthaleïn and methyl-orange. The sp. gr. of the product dried at  $200^\circ$  is 4.216 at  $24^\circ$ .

The determination of the atomic weight is carried out as follows. The finely-powdered material contained in a platinum boat is heated at  $200^\circ$  in a current of pure, dry air, then in a mixture of hydrogen bromide, nitrogen, and hydrogen at a red heat, and finally the excess of hydrogen bromide is driven over by a current of dry nitrogen and hydrogen. The hot boat is transferred as quickly as possible to a weighing glass, allowed to cool, and weighed. The ratio of silver to strontium bromide is determined as follows.

*1st Series.*—A small excess of silver is dissolved, diluted with about 100 times the amount of water, and the strontium bromide is shaken with it in a stoppered flask. The precipitate is separated by means of a Gooch's crucible, and the excess of silver estimated in the filtrate by Volhard's method. The mean of four experiments gave the atomic weight  $\text{Sr} = 87.644$ .

*2nd Series.*—The ratio is determined by titration with very dilute solutions of silver and hydrogen bromide according to the method described by Abrahall (*Trans.*, 1892, 662). The mean of four experiments gave the value  $\text{Sr} = 87.663$ .

*3rd Series.*—Pure silver bromide when shaken with water dissolves to a slight extent, and the filtrate gives a faint opalescence both with silver solution and with hydrobromic acid. Slightly less silver

solution than is required for the complete precipitation is added to the strontium bromide; and then a very dilute solution of silver (1 c.c. = 1 milligram Ag) is added drop by drop until two equivalent solutions of silver and hydrogen bromide produce an opalescence of equal intensity in the clear supernatant liquid. The mean of four experiments gave the value  $Sr = 87.668$ .

The ratio of silver bromide to strontium bromide is determined by precipitating the strontium bromide with a slight excess of silver nitrate. The precipitate is collected in a Gooch's crucible and treated by the usual method. The mean of seven experiments gave the value  $Sr = 87.6595$ .

The mean of all the experiments, discarding those obtained in the 1st Series, gave the value  $Sr = 87.663$  when  $O = 16$ .

E. C. R.

**Basic Nitrates.** By NICOLAS ATHANASESCU (*Bull. Soc. Chim.*, 1894, [3], 11, 1112—1114).—Certain metallic nitrates, when heated in sealed tubes at suitable temperatures, are converted, like sulphates and selenates, into basic salts. Thus, when the solution formed by boiling concentrated aqueous copper nitrate with excess of copper carbonate is heated for several hours at above  $300^{\circ}$ , a basic copper nitrate separates in small, emerald-green crystals, insoluble in water, but soluble in acids. The analytical results agree fairly well with those required by Gerhardt's formula,  $Cu(NO_3)_2 \cdot 3CuO, 3H_2O$ , which, in order to account for the tenacity with which the third molecule of water is held, may also be written as  $OH \cdot NO(O \cdot Cu \cdot OH)_2$ .

JN. W.

**Precipitation of Metallic Lead.** By J. B. SENDERENS (*Bull. Soc. Chim.*, 1894, [3], 11, 1163—1165).—The small globules of metallic lead deposited on a rod of that metal immersed in a solution of its nitrate, are not formed when the acetate is substituted for the nitrate.

The phenomenon is probably electrolytic, and may be explained by supposing that in casting the rod, its central and peripheral portions assume different physical states, owing to the difference in the rates of cooling. The difference of potential thus set up between different parts of the rod will then cause the passage of local currents through the solution.

In confirmation of this view, it is to be observed that a strip of lead, one side of which is polished and the other roughly crystalline, decomposes lead nitrate much more quickly than a strip polished entirely, the characteristic yellow colour of the nitrosonitrate appearing almost at once, whilst metallic lead and subsequently basic lead nitrate (next page) are precipitated. Since acetic acid is not capable of reduction under these conditions, the action does not take place in a solution of lead acetate.

JN. W.

**Preparation of Lead Dioxide.** By WILHELM MINOR (*Chem. Centr.*, 1894, ii, 412; from *Techniker*, 16, 80).—Lead oxide is introduced in the requisite amount of melted sodium hydroxide, and the necessary quantity of sodium nitrate is then added. The products of

the fusion are sodium nitrite and plumbate, which, on boiling with water, yields a precipitate of lead dioxide of great purity.

L. DE K.

**Lead Orthonitrate.** By J. B. SENDERENS (*Bull. Soc. Chim.*, 1894, [3], 11, 1165—1166).—*Basic lead nitrate*,  $N_2O_5 \cdot 2PbO \cdot 1\frac{1}{2}H_2O$  (preceding page), crystallises from hot water in monoclinic needles, and is quite stable in air; it loses  $\frac{1}{2}H_2O$  at  $100^\circ$  and the remainder at  $190^\circ$ . If the latter be regarded as water of constitution, the formula may be written  $N_2O_5 \cdot H_2O \cdot 2PbO + \frac{1}{2}H_2O$  or  $Pb_4H_1(NO_4)_4 + H_2O$ , thus representing the salt as a hydrated form of a lead hydrogen orthonitrate,  $PbHNO_4$ , corresponding with the acid orthophosphates of bivalent metals.

JN. W.

**Thallium Hydrogen Carbonate.** By GIOVANNI GIORGIS (*Gazzetta*, 1894, 24, ii, 474—479).—On passing a current of carbonic anhydride for 2—10 weeks through a fairly concentrated solution of thallous oxide contained in a closed vessel over sulphuric acid, *thallium hydrogen carbonate*,  $TlHCO_3$ , is slowly deposited in needles. The pure substance was only obtained on one occasion by this method, the other preparations containing rather too much thallium; the conclusions of Lamy and Des Cloizeaux and of Jörgensen respecting the existence of this salt are partially erroneous.

W. J. P.

**Action of Dry Hydrogen Chloride on Serpentine.** By REINHARD BRAUNS (*Zeit. anorg. Chem.*, 1895, 8, 348—351).—An answer to E. A. Schneider (this vol., ii, 166). The hydrogen chloride employed by Clarke and Schneider was mixed with traces of water which influenced its action. The presence of water induced the action of the hydrogen chloride and brought about the decomposition of the magnesium silicate. Water is formed during the decomposition of the magnesium silicate, and this increases the action of the hydrogen chloride and produces a further decomposition. The manner in which the hydrogen is combined in minerals containing hydrogen cannot be determined by this reaction, nor can the number of the the  $Mg\cdot OH$ -groups from the amount of magnesium chloride obtained.

E. C. R.

**Action of Magnesium on Manganous Salts.** By JOSEPH G. HIBBS and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1894, 16, 822—823).—The authors have tried the action of magnesium on aqueous solutions of manganous chloride, both in the presence of alcohol and of alcohol and ether, with the object of reducing the oxidation of manganese, if any should appear, to a minimum. It has not, as yet, been satisfactorily solved whether the deposit contained metallic manganese or a kind of hydrated oxide. The fact that the sum total of the constituents of the products of the action—chlorine, magnesium, and manganese—are less than the quantity of material taken for analysis favours the latter theory.

L. DE K.

**Chemical Character of Pyrites and Marcasite.** By AMOS P. BROWN (*Chem. News*, 1895, 71, 120—121, 131—132, 144—145, 155,



171—172, 179—181).—The author has investigated the two varieties of iron bisulphide found in nature, the brass-yellow pyrites and greyish-yellow or pale green marcasite; the former resists the action of air, and, when decomposed in the earth, gives rise to limonite frequently in pseudomorphs, whereas the latter oxidises readily, yielding generally ferrous sulphate and only occasionally limonite; pyrites is obtained when ferrous sulphide is deprived of iron by ferric salts or carbonic acid, marcasite when ferrous sulphate undergoes reduction by organic matter; the former has been obtained artificially. Specially selected pure specimens of each mineral were used in these experiments. They were shaken at intervals of 15 minutes, in a finely pulverised condition, with neutral aqueous solutions of potassium permanganate of four strengths, namely N/100, and 1, 3, and 5 per cent., for periods of one, two, three, four, and five hours, and at ordinary temperatures and at 100°, each particular test being repeated 10 times. After the solutions had acted for the required time, the sulphuric acid was determined in the solutions. Marcasite in most cases oxidised rather more quickly than pyrites, but in none of the experiments did the amount of sulphur oxidised reach the proportion oxidised in pyrites by electricity, by which agent all the sulphur of marcasite is oxidised readily, whilst less than half the sulphur of pyrites is attacked. No definite results were obtained by treating the two minerals with hydrochloric or sulphuric acid, cold, hot, dilute, or concentrated, nor with dry hydrochloric acid at 210°; but with the latter at 310°, 325°, or at a red heat, pyrites was more vigorously attacked than marcasite. In a current of ammonium chloride in an atmosphere of nitrogen at 335°, marcasite yielded ferrous chloride, pyrites the ferric salt, with small loss of sulphur in both cases. Heating at 200° with copper sulphate solution in sealed tubes, marcasite yielded a solution wholly ferrous, but with pyrites only 19.9 per cent. was ferrous, the rest ferric. Hence pyrites appear to have the composition  $4\text{Fe}^{\text{IV}}\text{S}_2, \text{Fe}^{\text{II}}\text{S}_2$ , marcasite, on the other hand, to be  $\text{Fe}^{\text{II}}\text{S}_2$ , or a polymeride of it.

D. A. L.

**New Nitroso-compounds of Iron.** By KARL A. HOFMANN and O. F. WIEDE (*Zeit. anorg. Chem.*, 1895, **8**, 318—322).—*Potassium dinitrosoferrothiosulphonate*,  $\text{Fe}(\text{NO})_2\text{S}_2\text{O}_3\text{K}, \text{H}_2\text{O}$ , is obtained by passing nitric oxide into a concentrated aqueous solution of ferrous sulphate and potassium thiosulphate at the ordinary temperature. The solution turns dark brown, and then reddish-brown, metallic-looking plates of the new compound being precipitated; after drying in a vacuum over sulphuric acid, it has the above composition. It is sparingly soluble in water, but a small trace is sufficient to colour the water an intense yellow. In concentrated sulphuric acid, it dissolves, with an intense, greenish-yellow colour. The solution shows an absorption of blue and violet light of  $\lambda = 514$ , and, when heated, turns rose-red and decomposes. Alkalis decompose it only when warm, ammonia decomposes it at once. It is decomposed by hydroxylamine in the presence of alkali with evolution of gas and separation of ferrous hydroxide.

The *sodium salt*,  $\text{Fe}(\text{NO})_2\text{S}_2\text{O}_3\text{Na} + 2\text{H}_2\text{O}$ , closely resembles the potassium salt, but is more soluble in water and alcohol, and gives an

intense, brown solution. The alcoholic solution shows a characteristic absorption band  $\lambda = 585$ , and a more intense absorption of  $\lambda = 516$ . It is stable at  $0^\circ$ , but at the ordinary temperature evolves small quantities of nitric oxide.

The *ammonium salt* with  $1\text{H}_2\text{O}$  crystallises in lustrous, black leaflets, and is much more stable than either the potassium or sodium salts. It can be crystallised from warm water without decomposition, and separates in large, lustrous, black plates.

The authors have obtained similar salts containing cobalt or nickel, and are engaged in their examination.

E. C. R.

**Atomic Weights of Nickel and Cobalt.** By CLEMENS WINKLER (*Zeit. anorg. Chem.*, 1895, 8, 291—295).—The author has determined the atomic weight of iron by the method he employed for the determination of the atomic weights of nickel and cobalt (this vol., ii, 167). The iodine and other reagents employed were prepared exactly according to the method previously described. With pure, clean iron wire containing 0.1 per cent. of carbon and 0.3 per cent. of silicon, sulphur, phosphorus, copper, &c., the mean of three experiments gave the atomic weight  $\text{Fe} = 56.0499$ . With the same iron, after heating it in a current of pure hydrogen for one hour, the mean of three experiments gave the atomic weight  $\text{Fe} = 56.0162$  ( $\text{H} = 1$ ). These values are so close to the values obtained by other chemists that the accuracy of the method employed and the purity of the reagents is placed beyond doubt.

E. C. R.

**Colloidal Gold.** By PAUL SCHOTTLÄNDER (*Chem. Centr.*, 1894, ii, 409; from *Verh. Vers. Deutsch. Ntf. Ärzte*, ii, 73—78).—The author prepares a deep violet-red solution which contains gold in a colloidal form as follows. To a solution of 15.75 grams of pure crystallised cerous oxalate in 300 c.c. of boiled water is gradually added, while shaking, 400 c.c. of N/10 soda, and then at once 300 c.c. of a neutral gold solution, prepared according to Thomsen's method and containing 2 grams of gold. The mixture is first heated on the water bath, and then freely boiled for 1—1½ hours. The solution, which otherwise is very permanent, is precipitated by bases, acids, and salts, with the formation of red or blackish-violet deposits; these separate but slowly leaving an apparently blue solution. The precipitates caused by neutral salts of the alkalis contain, besides gold, basic ceric acetate; when incompletely dried, they readily redissolve in water and alcohol, but, after drying at  $100^\circ$ , they become completely insoluble. If a slightly acid solution of sodium acetate is added and the precipitate be redissolved in water and again reprecipitated, it will each time become richer in gold and poorer in cerium; but after repeated precipitation the compound becomes at last insoluble in water, and then contains about 53.7 per cent. of gold and 39.32 per cent. of cerium oxide, the remainder being combined acetic acid and water. The two metals cannot be separated by dialysis, as the cerium compound also exists in the colloidal form.

L. DE K.

**Double Chlorides of Alkali Metals with Gold ; Separation of the Alkalis from each other.** By R. FASBENDER (*Chem. Centr.*, ii, 609 ; from *Ned. Tijds. Pharm.*, 1894, 6, 227—229 ; compare *Abstr.*, 1894, ii, 421).—The double chlorides of gold with potassium and rubidium differ from each other in their solubility in alcohol. The potassium salt dissolves in about four parts of 98 per cent. alcohol, whilst the rubidium salt requires about 54 parts. This distinction can be applied to the preparation of rubidium salts free from potassium. The rubidium salt, when dried at 100°, has the composition  $\text{AuCl}_3\text{RbCl}$  ; after reduction by means of oxalic acid, the rubidium can be determined as carbonate.

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A. G. B.

## Mineralogical Chemistry.

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**Monazite from North Carolina.** By H. B. C. NITZE (*Chem. News*, 1895, **71**, 181).—Monazite is found in various parts of North and South Carolina, the best crystallised specimens at Milholland's Mill and Stoney Point, Alexander Co. It occurs in stream sands and gravels, 1 ft. to 2 ft. thick, associated with quartz, felspar, hornblende, epidote, mica, magnetite, garnet, zircon, rutile corundum, &c., the primary source being crystalline gneisses and schists, of which it is an accessory constituent. The percentage of thorium varies, the transparent, greenish- and yellowish-brown varieties being stated to be the richest; at Brindletown, Burke Co., North Carolina, the sand runs from 4 to 6.6 per cent., near Shelley, in Cleveland Co., 2.76 per cent. It is separated by washing. D. A. L.

**Chemical Composition and Constitution of Vesuvians.** By PAUL JANNASCH and P. WEINGARTEN (*Zeit. anorg. Chem.*, 1895, **8**, 356—363).—The paper contains the results of the complete analysis of nine specimens of vesuvian. One series of these vesuvians contained fluorine; in the other, the fluorine is completely replaced by hydroxyl. The iron is present partly in the form of oxide; small quantities of manganese, potassium, sodium, and lithium are present even in the purest specimens, and occasionally rarer elements, such as titanium, occur. The results obtained are in accordance with the composition  $(\text{SiO}_4)_2\text{Al}(\text{Fe}, \text{Ti})\text{Ca}_2(\text{Mg}_2, \text{Fe}_2, \text{Mn}_2)\text{H}(\text{K}, \text{Na}, \text{Si})$ , or  $\text{Si}_4\text{O}_{14}\text{Al}_2\text{Ca}_4(\text{OH})_2$ . E. C. R.

**Cañon Diablo Meteorite.** By ORVILLE A. DERBY (*Amer. J. Sci.*, 1895, [3], **49**, 101—110).—A meteoric individual weighing 195 grams was treated with cold hydrochloric acid of strength 1 to 10; analysis of the 92.95 per cent. (neglecting vein matter and a jagged nuclear piece) dissolved is given under I; this agrees with kamacite,  $\text{Fe}_{14}\text{Ni}$ . The residue was separated into groups; the analysis of the tænite is given under II (there being also 1.65 per cent. of schreibersite); III is one of the analyses given of the cohenite. Three forms of iron nickel phosphide occur, two of which, namely, acicular rhabdite

and granular schreibersite, are probably identical; an analysis of a third form, strongly resembling mispickel in appearance, is given under IV; another analysis of the same shows 1.18 per cent. of tin. The non-magnetic portion of the residue was also examined.

	Fe.	Ni.	Co.	P.	Cu.	C.
I.	91.26	8.25		0.44	0.04	—
II.	66.46	30.28	0.68	0.30	0.32	—
III.	92.88	1.33		0.48	—	5.33
IV.	54.34	31.48	0.67	12.82	0.20	—

The occurrence of diamond in this meteorite (Abstr., 1894, ii, 195) is not confirmed. L. J. S.

**Plymouth Meteorite.** By HENRY A. WARD (*Amer. J. Sci.*, 1895, [3], 49, 53—55).—The extreme dimensions of this meteorite, found in 1893, in Indiana, are given as  $12\frac{1}{2} \times 7\frac{3}{8} \times 2$  in. Analysis gave—

Fe.	Ni.	Co.	Cu.	P.	Graphite.	S.
88.67	8.55	0.66	0.24	1.25	0.11	0.07

Small nodules of troilite occur embedded in the iron. A larger mass from the same locality, which has been lost, is mentioned.

L. J. S.

### Physiological Chemistry.

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**Absorption of Fat.** By VAUGHAN HARLEY (*J. Physiol.*, 1895, 18, 1—14).—From experiments made on dogs, the following conclusions are drawn. Under normal circumstances, a dog absorbs from 9 to 21 per cent. of the total fat given in 3 to 4 hours; from 21 to 46 per cent. in 7; and 86 per cent. in 18 hours. The passage of fat from the stomach to the intestines varies with the individual, and with the time allowed for digestion. In 3 to 4 hours, 25 to 44 per cent. of the fat given has left it; in 7 hours, 33 to 63 per cent.; whilst in 18 hours all has entered the intestines. Of the fat that has actually entered the intestines, and therefore is under favourable circumstances for absorption; 37 to 76 per cent. is absorbed in 3 to 4 hours; 65 to 86 per cent. in 7 hours; and 86 per cent. in 18 hours.

In dogs which have had their pancreas removed, the quantity of fat given is not only again recovered, but a surplus is found which is probably derived from the intestinal secretion. The passage of fat from the stomach is very much delayed by extirpation of the pancreas. Such dogs pass in 4 to 6 hours 3 to 10 per cent. of the fat given into the intestines, whilst in 7 hours only 9 to 22 per cent. has traversed the pylorus.

W. D. H.

**Absorption of Salt Solutions from the Pleural Cavities.** By J. B. LEATHES and ERNEST H. STARLING (*J. Physiol.*, **18**, 1895, 106—116).—Heidenhain (*Pflüger's Archiv.*, **56**) showed that absorption from the intestine is not simple osmosis, but that if the epithelium is paralysed by sodium fluoride, the absorption of salt solutions follows the ordinary laws of osmosis. The present experiments, which were performed on dogs, were made on this model; sodium chloride was the salt chiefly used, but experiments with other salts gave corresponding results. Absorption was found to obey the laws of osmosis; there was no evidence of vital action of the pleural endothelium, as the cells behave in the same way after being scalded or poisoned with sodium fluoride as in the normal condition. A small absorption of fluid by the lymphatics, due to the mechanical movements of the lung, has also to be reckoned with. W. D. H.

**Action of Copper on the Animal Organism.** By MAX KLEMPNER (*Chem. Centr.*, 1894, ii, 620; from *Pharm. Zeit. Russ.*, 1894, **33**, 485—487).—The author used a solution of sodium cupric tartrate containing 0.0217 gram of copper oxide per c.c., and incapable of precipitating serum-albumin. With hæmoglobin, this solution yields a compound which is insoluble in water; in the case of ox's blood, pig's blood, and pigeon's blood, 1 gram of hæmoglobin will be precipitated by 0.035 gram of copper; in the case of dog's blood, cat's blood, and the blood of dead animals, the same proportion does not prevail.

For the estimation of small quantities of hæmoglobin, 0.1 c.c. of blood may be dissolved in 30 c.c. of water, and titrated with very dilute copper solution, until the filtrate is quite clear. Excess of copper in the filtrate may be detected by the addition of filtered dilute blood solution, when so little as 0.015 milligram of copper oxide will give a precipitate.

"Kupferhämol" is copper hæmoglobin, and behaves like "zinkhämol," which, according to Kobert, is a zinc parahæmoglobin. Copper hæmoglobin contains 2 per cent. of copper; it is insoluble in dilute alcohol, and in neutral solutions of alkali salts, but dissolves in dilute organic and inorganic acids, which, however, gradually decompose it. Organic and inorganic bases colour copper hæmoglobin solution red, and the liquid shows the oxyhæmoglobin spectrum; when dissolved in potassium cyanide or ammonium hydrogen sulphide, it shows the hæmochromogen spectrum, and in sulphuric acid it shows the hæmatoporphyrin spectrum. Water which has been shaken with turpentine dissolves copper hæmoglobin forming a brilliant red solution.

The following symptoms are to be noticed in poisoning by sodium cupric tartrate. Atrophy, both in acute and chronic cases; diarrhœa, some time before death, and persistent vomiting, in chronic cases; enfeebled pulse and laboured respiration. When subcutaneously injected in the pleura, the salt produces weakness and stiffness of the hinder extremities; the same is noticed when the salt or copper hæmoglobin is exhibited. In one case, blood and albumin were found

in the urine; copper was not found in the blood serum, but in the blood corpuscles.

A. G. B.

**Poisoning by Barium Salts.** By ANGIOLO FUNARO (*L'Orosi*, 1894, 17, 397—403).—Particulars are given of the symptoms and post-mortem appearances in a case of poisoning by 30—50 grams of barium chloride taken internally. Small quantities of the metal were separated from the stomach, both in a soluble and insoluble form; a small quantity of soluble barium salt was also isolated from the liver, showing that the poison had been absorbed by the system. The metal was also found in the heart, the muscles, and the kidneys.

W. J. P.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Enzyme of *Schizosaccharomyces Octosporus* and of *Saccharomyces Marxianus*.** By EMIL FISCHER and PAUL LINDNER (*Ber.*, 1895, **28**, 984—986).—So far as it has at present been ascertained, it appears probable that the fermentation of the polysaccharides by saccharomycetes is preceded by their conversion into monosaccharides through the agency of enzymes (compare this vol., i, 6 and 161). It was therefore to be expected that *Schizosaccharomyces Octosporus*, which, according to its discoverer, Beyerinck (*Centr. Bacter.*, **12**, No. 2, 49), ferments maltose, but not saccharose, secretes a glucase (maltase), but no invertase, and this hypothesis has been verified by experiment. A pure culture of the yeast was washed with water, dried on a porous plate, at the temperature of the room for three days, pulverised, and digested with 20 parts of water for 20 hours at 33°. The clear, filtered extract was found to have no action on saccharose; when, however, maltose (1 part) was treated with the extract (10 parts) for 20 hours, at 33°, both in presence of chloroform and otherwise, the phenylhydrazine test indicated the production of more glucosazone than maltosazone.  $\alpha$ -Methylglucoside was also hydrolysed by the extract, but the reaction proceeded somewhat more slowly than in the case of maltose. The authors have not yet succeeded in isolating the enzyme.

*Saccharomyces Marxianus*, according to Hansen, ferments saccharose, but not maltose. The observation of Fischer and Thierfelder (*Ber.*, **27**, 2031), that this yeast ferments maltose, is now found to be incorrect. An aqueous extract of the air-dried yeast hydrolyses saccharose completely, but has no appreciable action on maltose.

A. R. L.

**Behaviour of Yeast towards Glycogen.** By ALFRED KOCH and HANS HOSAEUS (*Chem. Centr.*, 1894, ii, 869; from *Centr. Bacter. und Parasitenk.*, 1894, **16**, 145—148).—To test Errera's hypothesis and the generally accepted opinion concerning the self-fermentation of yeast, the authors have tried whether yeast can make use of animal glycogen added to an artificial nutrient solution. For this purpose,

Frohberg yeast, compressed yeast, and beer-yeast were grown in a solution containing 0.5 per cent. of glycogen. It was found that the presence of the glycogen did not increase the growth of the yeast; the small quantity employed did not diminish, even after a long time, under the influence of the yeast, but the diverse bacteria which accompanied impure cultures speedily decomposed it, so that the nutrient solution soon failed to show the glycogen iodine reaction. No glycogen was found to have been formed in the yeast cells at the expense of the added glycogen, and very little alcohol was produced. Even Frohberg yeast, which is able to ferment maltodextrins, behaves towards glycogen in the manner described. Each of the three kinds of glycogen used (that from the dog and the calf, and from yeast) diminished the yeast harvest and the quantity of alcohol produced, both in very poor (flesh extract) and in very good (beer-wort) nutrient solutions; qualitatively, there appeared to be no difference between the action of the three kinds, but quantitatively there was a slight difference.

These experiments show that in the solutions employed, yeast does not give rise to a diffusible ferment, which can so act on animal or yeast glycogen as to produce a fermentable, diffusible substance. On the other hand, the question remains open whether the yeast can make use of the glycogen which exists within itself. A. G. B.

**Cell-membrane of Fungi.** By EUGÈNE GILSON (*Chem. Centr.*, 1894, ii, 874—875; from *La Cellule*, 1894, 11, 7—15).—*Claviceps purpurea* was treated according to the method for obtaining E. Schulze's cellulose (*Abstr.*, 1891, 1178; 1892, 907). The finely-powdered material, freed from fat, was treated several times with a 0.5 per cent. soda solution, washed with water until the washings were no longer alkaline, and heated for six hours with a 2½ per cent. sulphuric acid solution. After the residue had been washed with water, it was left in contact with a mixture of 12 parts of nitric acid (sp. gr. 1.15) and 1 part of potassium chlorate for 14 days. The acid was then washed away, and the residue digested at 60° for one hour with very dilute ammonia, and finally washed and dried.

The product is coloured neither by iodine and strong sulphuric acid nor by zinc chloride containing iodine; it is insoluble in Schweizer's reagent, and is entirely different from cellulose. To ascertain whether the substance is a mixture or a compound of cellulose with another substance, it was treated, according to Hoppe-Seyler's method, with caustic potash, and then washed with water, whereby the cellulose was left. The product obtained in this way from *Claviceps purpurea* is coloured by iodine and sulphuric acid, but is totally different from cellulose. It is insoluble in Schweizer's reagent and in hydrochloric acid of medium strength, but it dissolves in cold, very dilute hydrochloric acid, and this solution is precipitated by a few drops of strong acid. It also dissolves in warm dilute sulphuric acid, but separates again when the solution is cooled. This substance, which is nitrogenous, and is also obtainable from *Agaricus campestris*, is called mycosin by the author.

*Mycosin*,  $C_{14}H_{28}N_2O_{10}$ , is best prepared by precipitating a solution

of its crystalline hydrochloride by potash; it then forms an amorphous, granular, yellowish-white precipitate. It is only coloured by iodine and sulphuric acid and by iodine and zinc chloride when these reagents are sufficiently dilute. The *hydrochloride*,  $C_{14}H_{28}N_2O_{10} \cdot 2HCl$ , is a white, slightly-reddish powder, which appears crystalline under the microscope, and is active towards polarised light; it is soluble in water, but not in alcohol; it is not coloured by reagents containing iodine. The *sulphate* is very similar, but is only soluble in hot water

A. G. B.

**The Place of Tannins in Plant Metabolism.** By G. MIELKE (*Ann. Agron.*, 1895, **21**, 87—88; from *Progr. d. Realschule v. d. Holzthore in Hamburg*, 1893).—The phenols, with their acids and anhydrides (wrongly termed tannic acids, owing to their reaction with iron salts and potassium dichromate), which occur in nearly all plants, are derived from carbohydrates. Alcohols and aldehydes are formed as intermediate products, the importance of which is indicated by their presence in the cambium layer of plants. There is no evidence showing that the tannins can be produced from proteids. In their formation from carbohydrates, the phenols, phenol-alcohols, and aldehydes migrate in combination with sugar, and play an important part in furnishing the materials necessary for covering the wood. The tannic substances are deposited in relatively small quantities in the body of the plant. By the formation of anhydrides, by oxidation, and by dry distillation, they could furnish, on the one hand, phlobaphenes (colouring matters of the bark), on the other, the substances which transform albumum into duramen. The resins and ethereal oils would be the final products of the tannins.

N. H. J. M.

**Analyses of Norwegian Hay Grasses.** By F. H. WERENSKIÖLD and E. SOLBERG (*Bied. Centr.*, 1895, **24**, 165—167; from *Tidsskr. Norsk. Landbr.*, 1894, **1**, 190—198).—Analyses of the following grasses, grown in a sandy soil not far from Christiana, were made:—(1) *Phleum pratense*, (2) *Festuca elatior*, (3) *Avena elatior*, (4) *Dactylis glomerata*, (5) *Agrostis stolonifera*, (6) *Bromus arvensis*, (7) *Alopecurus pratensis*. The following percentage results are given.

Water.	Ash.	Crude protein.	Crude fibre.	Crude fat.	N.-free extract.	Digestibility of protein.
1. 15·00	4·01	4·75	26·91	1·84	47·49	74·35
2. 15·29	5·36	5·34	27·29	2·17	44·45	75·3
3. 16·91	4·45	5·19	25·33	1·99	46·13	85·6
4. 17·52	6·88	6·82	26·28	3·00	39·40	78·25
5. 16·54	5·09	7·07	27·07	1·94	42·29	68·5
6. 16·44	3·71	4·19	29·60	1·50	44·56	77·6
7. 12·42	6·50	7·63	28·37	2·81	42·77	75·8

The number of samples analysed were: No. 1, four; No. 2, three; No. 4, six; No. 5, two; the rest one each (compare König, *Zusammensetz. u. Verdaulichkeit d. Futtermittel*).

N. H. J. M.

## Analytical Chemistry.

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**Nitrocellulose Filters.** By HENRY N. WARREN (*Chem. News*, 1895, **71**, 165).—To facilitate filtration and incineration during the examination of phosphates and similar precipitates, it is suggested that ashless filter-papers should be immersed separately for five minutes in a mixture of nitric acid, sp. gr. 1.5, with an equal volume of good oil of vitriol, to obtain a rapidly-burning paper insoluble in ether; whilst, to obtain a paper burning with less rapidity and soluble in ether, a mixture of ordinary nitric acid with twice its volume of vitriol should be used, and the last mixture, with the addition of a small quantity of hydrofluoric acid, should be employed for the treatment of ordinary filter-papers. The papers must be washed free from acid, carefully dried, and preserved in stoppered bottles.

D. A. L.

**Some Indicators.** By P. A. BOORSMA (*Chem. Centr.*, 1894, ii, 447; from *Ned. Tydschr. Pharm.*, 1894, **6**, 205—213).—Phosphoric acid may be considered as a mono-, di-, or tri-basic acid, according to the nature of the indicator, methyl-orange (or cochineal), phenolphthaleïn, or Poirrier's blue. The results differ slightly when alkaline earths are used instead of alkalis. The titration with lime and rosolic acid is very accurate if the solution is well boiled. Litmus is not to be recommended, as it is carried down with the precipitate. Borates soon dissociate even in fairly concentrated solutions. Boric acid does not affect methyl-orange, but it sensibly acts on litmus and phenolphthaleïn. Using Poirrier's blue, it may be titrated as a monobasic acid, but it is best done in presence of at least 25 per cent. of glycerol.

Regarded in the nature of feeble acids, the indicators may be classified as follows:—Methyl-violet, methyl-orange, dimethylamido-benzene, congo, lacmoid, carminic acid, phenacetolin, azolitmic acid, rosolic acid, phenolphthaleïn, turmeric, and Poirrier's blue.

L. DE K.

**A New Process for Drying Hygroscopic Substances.** By KARL ZULKOWSKI and ENRICO PODA (*Chem. Centr.*, 1894, ii, 532—533; from *Ber. Österr. Ges. Chem. Ind.*, **16**, 92—98).—The following process is recommended for the complete drying of such substances as molasses, invert sugar, and the like:—10 grams of the sample is mixed with 50 c.c. of methylic alcohol in a flask connected with an air-pump, and then heated. The alcohol soon boils off, carrying over all the water. The remaining spirit and traces of moisture are then removed by passing a current of dried air for about half an hour.

L. DE K.

**Estimation of Water in Silicates.** By PAUL JANNASCH and P. WEINGARTEN (*Zeit. anorg. Chem.*, 1895, **8**, 352—355).—The method consists in heating the finely-powdered silicate mixed with dry borax in a tube of hard glass, and passing over it a current of dry air. If the silicate contains fluorine, the gases are passed through a column of

dry lead chromate before absorbing the water. The combustion tube is bent in the centre so as to form a reservoir about 7 cm. long in which the mixture of silicate and borax is heated, and so that the outlet for the gases is constricted. The tube charged with borax is heated in a muffle at  $270-280^{\circ}$  for half an hour, a current of dry air being passed through it at the same time. It is then allowed to cool slowly, and the silicate introduced and mixed with the borax. The mixture is then heated until all the water is expelled, the water being collected in a weighed calcium chloride tube. E. C. R.

**Estimation of Halogens in Organic Compounds.** By JAMES WALKER and JAMES HENDERSON (*Chem. News*, 1895, **71**, 103).—The substance is heated in the ordinary way, in a sealed tube, with fuming nitric acid and silver nitrate, but the latter is employed in quantities in excess of that required to form a silver salt with all the halogen of the compound, and, moreover, is weighed accurately; so that at the close of the reaction, instead of weighing the silver chloride, the contents of the tube are washed into a flask, boiled to expel lower oxides of nitrogen, and the excess of silver nitrate is titrated with ammonium thiocyanate, using iron alum as an indicator; by this means, the amount of halogen present is easily ascertained. The thiocyanate is standardised against a portion of the silver nitrate used in the precipitations. D. A. L.

**Estimation of Chlorine in Wool Grease.** By P. LOHMANN (*Chem. Centr.*, 1894, ii, 901; from *Pharm. Zeit.*, **39**, 707—708).—The author has tested Benedikt's recent process and found that but little of the chlorine is absorbed by the lime, the greater part being lost in the gaseous products or the tarry matter. The following process is recommended:—The melted fat is cautiously dropped upon fusing sodium nitrate and carbonate mixture, the dropping-tube being weighed before and after the operation. The melt is afterwards examined for chlorine as usual. Although no doubt a small quantity of chlorine escapes with the gases formed during the combustion, still the process gives decided amounts of chlorine where Benedikt's process gives but traces. L. DE K.

**Estimation of Chlorine in Wool Grease.** By RUDOLPH BENEDIKT (*Chem. Centr.*, 1894, ii, 902; from *Pharm. Zeit.*, **31**, 733).—A reply to Lohmann (preceding abstract), stating that in the author's recent process the fatty vapours are passed over two separate layers of ignited quicklime, and that the second layer was always found to be free from chlorine, showing the completeness of the absorption.

L. DE K.

**New Volumetric Method.** By J. KNOBLOCH (*Chem. Centr.*, 1894, ii, 533—534; from *Pharm. Zeit.*, **39**, 558—559).—The author's process is based on the following facts:—When a solution of ferric chloride is mixed with the equivalent quantity of potassium fluoride, the decomposition is complete, and the resulting ferric fluoride solution is colourless. In this state, the iron is not detectable by potassium thiocyanate, salicylic acid, acetates, antipyrin, &c. Still more

interesting is the fact that ferric fluoride does not liberate iodine from iodides. The following standard solutions are required:—

1. *N/10 solution of potassium fluoride*; 5·809 grams of the ignited salt is dissolved in water up to 1 litre. 2. *N/60 solution of ferric chloride*; 19·0 grams of officinal ferric chloride solution is diluted to 1 litre. 3. *N/30 solution of sodium thiosulphate* made by diluting the usual *N/10* solution with 2 vols. of water. 4. *Zinc iodide solution*; a mixture of 10 grams of iodine, 5 grams of zinc powder, and 25 c.c. of water is warmed until colourless, and then diluted to 40 c.c. This solution keeps better than potassium iodide solution.

1. *Estimation of Fluorine in Soluble Fluorides*.—The liquid is acidified with hydrochloric acid, and mixed with a known excess of ferric chloride solution, then with excess of zinc iodide, and allowed to remain in a closed vessel at 35—40° for half an hour; the liberated iodine is then titrated with the sodium thiosulphate solution. The volume of thiosulphate solution used is deducted from that of the ferric chloride, and the difference is the measure for calculating the fluorine, 1 c.c. of thiosulphate representing 0·0019 gram of the latter.

2. *Estimation of Calcium and Strontium in their Soluble Salts*.—The liquid, which should contain free hydrochloric acid, is mixed with excess of potassium fluoride solution, and then with the same volume of ferric chloride solution. After adding a sufficiency of zinc iodide and heating, as before, for half an hour at 35—40°, the liberated iodine is titrated. One c.c. of thiosulphate = 0·002 of calcium. Lime in drinking-water may be estimated in this manner, before and after boiling. Nitrous acid should be estimated and allowed for, as it also liberates iodine.

L. DE K.

**Estimation of Sulphur in Urine.** By HENRI MOREIGNE (*Bull. Soc. Chim.*, 1894, [3], 11, 975—977).—The residue obtained by evaporating urine is fused in a porcelain crucible with a mixture of sodium nitrate and carbonate, and the sulphate in the product estimated in the usual way. The crucible does not break on cooling if sodium nitrate is used, although it is liable to do so when potassium nitrate is substituted for it.

JN. W.

**Estimation of Total Nitrogen in Urine.** By HENRI MOREIGNE (*Bull. Soc. Chim.*, 1894, [3], 11, 959—975).—Petit and Monfet's modification of Kjeldahl's method (*Abstr.*, 1893, ii, 343) is inaccurate, as the results vary with the amount of mercury used. The inaccuracy is partly due to the formation of tetramercurammonium sulphate, a substance which is precipitated by the caustic alkali, and not completely redissolved by the acid. If the mercury is omitted, the method is quite accurate, although distinctly more tedious.

JN. W.

**Estimation of Total Nitrogen in Urine.** By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1139—1142).—The modification of Kjeldahl's process, referred to by Moreigne (preceding abstract), appears to have been devised by Henninger in 1884, and subsequently modified by Kjeldahl and Borodin, and by the author.

The method as now recommended consists in heating a mixture of the

urine (10 c.c.) with concentrated sulphuric acid (5 c.c.) at 80° until the water is expelled, and then gradually raising the temperature until white fumes are evolved. When, after five or six hours, the liquid has become almost colourless, it is diluted (to 50 c.c.), and some of the solution (2.5 c.c.) washed into a gas measuring tube; after making alkaline with concentrated caustic soda (2 c.c.) it is decomposed with hypobromite. JN. W.

**The Gunning Method for Estimating Total Nitrogen in Fertilisers.** By W. E. GARRIGUES (*J. Amer. Chem. Soc.*, 1894, **16**, 795—799).—The Gunning method originally worked out for substances free from nitrates has of late been also recommended for manures containing the latter. Instead of simply boiling with potassium sulphate and sulphuric acid, some salicylic acid and some sodium thiosulphate must be added to the mixture.

To obtain fairly correct results, 1 gram of salicylic acid should be dissolved in 30 c.c. of sulphuric acid and mixed with about 2 grams of the sample contained in a 250—500 c.c. flask. Five grams of sodium thiosulphate is then added in four or five portions; when dissolved, 10 grams of potassium sulphate is added, and the operation is then conducted as usual. L. DE K.

**New Method for the Estimation of Nitrous Oxide.** By GEORGE T. KEMP (*Chem. News*, 1895, **71**, 108—111).—The method of estimating nitrous oxide by exploding or burning with hydrogen not being satisfactory, other means have been tried. Burning with carbon and exploding with carbonic oxide proved defective. But burning with considerable excess of carbonic oxide (7 : 1) and absorbing the carbonic anhydride formed has given good results when water is not present in excess of that required to saturate the gases, as the water suffers decomposition and the liberated hydrogen seems to enter into some condensible combinations, and high numbers are then obtained. The mixed gases are burnt over mercury in a grisometer by means of a spiral of platinum wire heated by an electric current.

D. A. L.

**Estimation of Phosphorus in Coal and Coke.** By LYCHENHEIM (*Chem. Centr.*, 1894, ii, 535; from *Trans. Amer. Inst. Min. Eng.*).—The ash left on incinerating the sample in a platinum dish, with constant stirring, is dissolved in 40 c.c. of hydrochloric acid, the solution evaporated to 10 c.c., mixed with 40 c.c. of nitric acid (sp. gr. 1.42), again evaporated to 20—25 c.c., and then diluted with water. After filtering from the silicic acid, the liquid is neutralised with ammonia and mixed with 40 c.c. of molybdate solution. The yellow precipitate is afterwards titrated. L. DE K.

**Estimation of Phosphorus in Iron.** By P. BÉNAZET (*Bull. Soc. Chim.*, 1894, [3], **11**, 1083—1091).—An account of the processes used in the various iron works on the Loire. The phosphorus, in nitric acid solution free from chlorine, is precipitated by molybdate at 45°, no arseniomolybdate being formed at that temperature. Large quantities of arsenic are best eliminated, however, as chloride. The ammonium phosphomolybdate is either weighed as such or as molyb-

denum phosphomolybdate, after ignition at 400—500°, or else estimated colorimetrically by the stannous chloride method, or volumetrically by oxidation with permanganate after reduction with zinc and boiling dilute sulphuric acid. JN. W.

**Volumetric Estimation of Official Phosphoric acid,** by JULIUS LANGER; and **Remarks on the same,** by CARL GLÜCKSMANN (*Chem. Centr.*, 1894, ii, 600—601; from *Pharm. Post*, 27, 369—370, 370—371).—Schneider and Geissler have stated that official phosphoric acid may be accurately titrated with standard soda (free from carbonate) using phenolphthaleïn as indicator, but the author did not obtain satisfactory results. Glücksmann's indirect process gave, however, exact results. This method consists in precipitating the acid with magnesia mixture containing a known amount of ammonia, and titrating the excess of the latter with N/10 oxalic acid, using litmus as indicator. Three mols of ammonia represent one mol. of trihydrogen phosphate. The magnesia solution is best prepared by dissolving 20 grams of magnesium sulphate and 10 grams of ammonium chloride in water, and adding 75 grams of ammonia. The whole is then made up to 500 c.c.

Glücksmann, in reply, states that the indirect process recommended by Maly gives, under favourable conditions, trustworthy results, but the precautions to be taken are so many that the method is quite unsuited for pharmaceutical purposes L. DE K.

**Estimation of Phosphoric acid by the Molybdate-Magnesia Method.** By B. W. KILGORE (*J. Amer. Chem. Soc.*, 1894, 16, 793—795).—A known quantity of crystallised sodium phosphate (dissolved in water) was sent to 28 analysts for the estimation of the phosphoric acid by the molybdate-magnesia method. The bulk of the analyses gave results decidedly in excess of the theoretical quantity, 19.826 per cent., in one case coming up to 20.67 per cent. Some, however, came very near to theory, and in their cases the magnesium precipitate had been purified by redissolving in hydrochloric acid and reprecipitating with ammonia. All the other precipitates contained no doubt an excess of magnesia.

Addition of a little citric acid before adding magnesia mixture also prevents precipitation of magnesium hydroxide. L. DE K.

**Estimation of Arsenic in Organic Matter.** By ERNEST BARILLOT (*Bull. Soc. Chim.*, 1894, [3], 11, 958—959).—A modification of Marsh's process. The organic matter having been destroyed by any of the well-known methods, the arsenic is precipitated as sulphide, and then oxidised by nitric acid and potassium nitrate. The nitric acid having been expelled by sulphuric acid at 200°, and the absence of nitrates and nitrites proved by means of brucine and metaphenylenediamine, the liquid is introduced by degrees into a Marsh's apparatus, the tube of which is heated in three distinct places. If the rate of evolution of hydrogen is properly adjusted, practically the whole of the arsenic is deposited in the first region, a



mere trace being precipitated in the second, and none at all in the third, thus rendering it certain that none has passed out of the apparatus. The operation is at an end when no further deposit takes place in the second and third regions on allowing the first region to cool. The sections containing the deposits are then cut out, and the arsenic weighed by difference.

JN. W.

**Estimation of Carbon in Iron.** By FRITZ FOERSTER (*Zeit. anorg. Chem.*, 1895, **8**, 274—290).—The paper contains a critical account of the methods usually employed. The method employed by the author consists in heating the sample of iron, either in the form of fine filings or in lump, with lead chromate in a current of dry air free from carbonic anhydride. A full description and drawing of the apparatus is given in the original paper; it consists essentially in a thick-walled porcelain retort having a capacity of about 50 c.c., and which can be heated at a temperature of 1500°. About 1—3 grams of iron and 30—50 grams of fused lead chromate are employed. The mixture is at first heated cautiously until all violent action is over, and then at the full heat of the furnace. The results obtained with irons containing 2 per cent. or less of carbon agree with those obtained by the usual methods, but with specimens of iron containing 4 per cent. or more of carbon, the results are higher.

E. C. R.

**Decomposition of Silicates by pure Lead Carbonate.** By PAUL JANNASCH (*Zeit. anorg. Chem.*, 1895, **8**, 364—367).—The lead carbonate employed is prepared by precipitating a hot solution of lead acetate with ammonium carbonate, and after washing the precipitate with water, drying it in a porcelain basin on the water bath. The silicate is mixed with 10—12 times the quantity of lead carbonate in a platinum crucible, and heated, at first gradually until the greater part of the carbonic anhydride is evolved, then at a red heat. The hot crucible and contents are thrown into cold water, treated with nitric acid, and the solution evaporated to dryness. The product is dissolved in nitric acid and water, separated from the insoluble silica, and the greater portion of the lead precipitated by the addition of concentrated hydrochloric acid. The salts are then converted into chlorides by evaporation with hydrochloric acid, and the remainder of the lead precipitated by hydrogen sulphide. The filtrate freed from hydrogen sulphide is then subjected to the ordinary methods for the separation of the metals.

E. C. R.

**The Hydrobromic acid Test for Copper.** By GEORGES DENIGÈS (*Bull. Soc. Chim.*, 1894, [3], **11**, 1024—1027).—Sabatier's proposed modification of the test by substituting phosphoric acid for the sulphuric acid is unsatisfactory, as the resulting solution is unstable. If the author's original directions be adhered to, and a saturated solution of potassium bromide mixed at a low temperature with half its volume of concentrated sulphuric acid, a reagent is formed which is quite stable and very sensitive, an addition of a trace of a copper compound in any form producing an intense, crimson

coloration. Any bromine which may be liberated after the lapse of time may be reduced by sulphite, without diminishing the sensitiveness of the reagent. JN. W.

**Acidimetric Estimation of Molybdic acid.** By KARL SEUBERT and WILLIAM POLLARD (*Zeit. anorg. Chem.*, 1895, 8, 296—301).—The method is as follows:—A weighed quantity of the substance to be analysed is dissolved in the smallest possible excess of semi-normal sodium hydroxide with the aid of heat, a very dilute solution of phenolphthalein is added and then semi-normal hydrochloric acid until the solution becomes colourless. The mixture is boiled for 10 minutes and titrated back to redness with the standard sodium hydroxide. With hydrated molybdic acid,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ , the mean of four experiments was 100.01 per cent. of that required by theory. With potassium trimolybdate,  $\text{K}_2\text{Mo}_3\text{O}_{10}$ , the reaction takes place according to the equation  $\text{K}_2\text{Mo}_3\text{O}_{10} + 4\text{NaOH} = \text{K}_2\text{MoO}_4 + 2\text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O}$ , and the results obtained agree with that required by theory. With molybdyl chloride,  $\text{MoO}_2\text{Cl}_2$ , prepared by heating molybdenum dioxide in dry chlorine, the reaction takes place according to the equation  $\text{MoO}_2\text{Cl}_2 + 4\text{NaOH} = \text{Na}_2\text{MoO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$ ; the mean of two experiments gave 64.47 per cent.  $\text{MoO}_3$ , instead of 64.45 per cent. With ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , the reaction takes place according to the equations  $3(\text{NH}_4)_2\text{MoO}_4 + 6\text{NaOH} = 3\text{Na}_2\text{MoO}_4 + 6\text{NH}_3 + 6\text{H}_2\text{O}$  and  $4\text{MoO}_3 + 8\text{NaOH} = 4\text{Na}_2\text{MoO}_4 + 4\text{H}_2\text{O}$ . Before titrating with acid, the mixture must be boiled until all the ammonia is expelled, and thus the ammonia may be estimated at the same time. The results agree with those required by theory. E. C. R.

**Quantitative Separation of Metals in Alkaline Solution by Hydrogen Peroxide.** By PAUL JANNASCH and A. RÖTTGEN (*Zeit. anorg. Chem.*, 1895, 8, 302—313).—*Separation of Bismuth and Cadmium.*—About 0.5 gram of each metal is treated with concentrated nitric acid (5 c.c.) and water, and the solution evaporated to dryness on the water bath; the dry product is then dissolved in nitric acid (5 c.c.) and water (25—30 c.c.) and poured into a solution of concentrated ammonia (15 c.c.) of 3 to 4 per cent. mixed with hydrogen peroxide (25—30 c.c.) (Abstr., 1894, ii, 482). The bismuth is completely precipitated as the hydrated peroxide, and carries down with it 0.5—0.6 per cent. of the cadmium; to separate this, the precipitate, after being washed with dilute ammonia and water, is redissolved in dilute nitric acid, and again precipitated and washed. The dried precipitate is removed from the filter-paper, which is incinerated and treated with nitric acid; the precipitate is then added, and the whole carefully heated in a platinum crucible until a constant weight is obtained. The bismuth oxide thus obtained contains any traces of silica which may have been present in the hydrogen peroxide, and this is estimated in the usual way. The cadmium is estimated in the filtrate by converting it into chloride and then precipitating with potassium carbonate. The precipitate is washed with cold water, dried at  $100^\circ$ , separated from the filter-paper, and

after igniting the latter, the whole is heated in a platinum crucible until a constant weight is obtained.

*The Separation of Lead and Cadmium* is effected in a similar manner to the above. The precipitate of hydrated lead dioxide which contains small quantities of cadmium is separated from the filter-paper and redissolved, the portions adhering to the filter-paper being dissolved in dilute nitric acid to which a small quantity of hydrogen peroxide is added. The lead is then again precipitated, and the precipitate treated in the same way as for bismuth.

*The Separation of Manganese and Copper* by this method requires more ammonia and hydrogen peroxide; 0.5 gram of copper sulphate and manganese sulphate dissolved in 30 c.c. of water and 10 c.c. of concentrated nitric acid are poured into 40 c.c. of ammonia and the same quantity of hydrogen peroxide solution, and the mixture warmed on the water bath. The hydrated manganese peroxide is washed with ammonia and hydrogen peroxide, redissolved, and again precipitated. The filtrate contains most of the silica, which is separated in the usual way; and finally the copper is precipitated by hydrogen sulphide and weighed as oxide.

Manganese and cadmium are separated in the same way as manganese and copper.

E. C. R.

**Separation of Bismuth, Lead, and Manganese from Mercury, by means of Hydrogen Peroxide.** By PAUL JANNASCH and E. v. CLOEDT (*Ber.*, 1895, **28**, 994—996).—The separation was carried out, as previously described (*Abstr.*, 1894, ii, 482), by pouring a solution of the mixed nitrates into dilute ammoniacal hydrogen peroxide. The bismuth, lead, or manganese is precipitated as a peroxide, and is free from silica if the hydrogen peroxide has been purified shortly before use by distillation under reduced pressure. The mercury is obtained by evaporating the filtrate in order to drive off the ammonia, making strongly acid with sulphurous acid, diluting, warming somewhat, and precipitating with hydrogen sulphide.

C. F. B.

**Diazobenzenesulphonic acid as a Reagent in Water Analysis.**

By J. J. COUVÉE (*Chem. Centr.*, 1894, ii, 930; from *Ned. Tydschr. Pharm.*, 1894, **6**, 313—317).—This reagent has been recommended to detect urine and excreta in water as it causes a yellow coloration when sewage is present.

The author, however, states that water containing iron also gives the reaction, so that this metal should be first tested for.

L. DE K.

**Estimation of Thiophen in Benzene.** By GEORGES DENIGÈS (*Compt. rend.*, 1895, **120**, 628—630; see this vol., i, 411).

**Anthracene Testing.** By HENRY BASSETT (*Chem. News*, 1895, **71**, 202—203).—Finding that chromic acid varies in quality, and in the quantity of sulphuric acid it contains, the author has tried the effect of these variations when testing anthracene. Good quality anthracene is but slightly affected, but with inferior qualities the results are

considerably affected by deficiency of chromic acid; this is, however, compensated for to a great extent by the presence of sulphuric acid. A considerable variation in the quantity of this latter acid has very little influence on the results.

D. A. L.

**Quantitative Testing of Ethereal Oils.** By SCHIMMEL (*Chem. Centr.*, 1894, ii, 899; from *Pharm. Zeit.*, 31, 735).—The estimation of the amount of ethereal salts (chiefly acetates) is often a good way of ascertaining the purity of ethereal oils. It must, however, first be ascertained whether the sample contains any aldehydes, for instance, cinnamaldehyde; should any be present it must be removed. Of the purified oil, 1—2 grams is boiled for 1—2 hours in a 100-c.c. flask attached to a reflux condenser with 10—20 c.c. N/2 alcoholic potash; the excess of alkali is then titrated and the ethereal salt calculated. This in conjunction with the sp. gr. will indicate whether a given oil is adulterated with turpentine, oil of lemon, &c.

To estimate the alcoholic constituents, 10—20 c.c. of the sample is boiled with an equal bulk of acetic anhydride, and 1—2 grams of anhydrous sodium acetate for 1—1½ hour in a reflux apparatus. After cooling, the contents is digested with water to dissolve the excess of acetic anhydride, and after introducing the mixture into a separating funnel, the oil is drawn off, dried over anhydrous sodium sulphate, and its amount of combined acetic acid estimated as directed. This is a valuable test, as some oils, although in most respects undistinguishable, differ very much in the amount of alcohols of high molecular weight that they contain.

L. DE K.

**Technical Analysis of Asphaltum.** By LAURA A. LINTON (*J. Amer. Chem. Soc.*, 1894, 16, 809).—The authoress, after due consideration of existing processes, recommends the following method of analysis:—A suitable portion of the sample is weighed in a four-ounce Erlenmeyer flask and treated over-night with 50 c.c. of light petroleum. The liquid is then decanted on a tared filter placed within a 3-in. funnel provided with a stop-cock in the neck. The residue is digested for a few hours with some more of the solvent, which is then again decanted; after repeating the operation until the liquid runs off colourless, the whole of the bitumen is transferred to the filter. The flask is dried in a steam bath and weighed, any increase being subtracted from the amount determined as petrolene. The filter is thoroughly washed with light petroleum, dried with its counterpoise in the steam bath, and weighed, the loss representing the petrolene.

The flask is thoroughly rinsed with boiling oil of turpentine and the liquid added to the filter in the closed funnel, the filter being wholly submerged under the liquid. The digesting and filtering is repeated until the filtrate becomes colourless. The turpentine is now in turn displaced by repeated washing with chloroform and the filter dried and reweighed; the loss in weight represents the asphaltene. The filter is now burnt and the mineral residue, after treating with ammonium carbonate, is then weighed, the loss on ignition representing other organic matter, or coke in the case of artificial asphalt.

L. DE K.

**Estimation of Mannitol in Wines.** By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1894, [3], 11, 1073—1080).—In quantities greater than 0.1 per cent., mannitol may be detected by evaporating the wine, when it is left in characteristic patches of radiating needles.

The optical method, of which an outline has already been given (this vol., ii, 141), is described in detail in the present paper. The wine (200 c.c.), after expulsion of the alcohol and removal of the sugars by fermentation with pressed yeast (2 grams), is evaporated to dryness, and the residue boiled for an hour with 90 per cent. alcohol (220—230 c.c.). The solution of mannitol thus obtained is separated from the insoluble gums and other substances, and allowed to crystallise.

If the percentage is large, the mannitol may be weighed as such, and the 10 per cent. or so remaining in the mother liquor calculated from the solubility.

If the percentage is not large, or if a more accurate result is required, the mannitol, after washing with absolute alcohol, is dissolved in water, and the solution, decolorised with animal charcoal, is examined polarimetrically, first alone, and then in the presence of borax, the percentage being calculated in the manner already described (*loc. cit.*). It is important that the liquid should be absolutely clear, and as nearly as possible colourless. The mother liquor is purified by means of basic lead acetate and animal charcoal, and examined polarimetrically in the same way. To correct for the lessened effect of the borax on the rotatory power in the presence of glycerol (*loc. cit.*) it is determined for a third time, after the addition of a known amount of mannitol. If the percentage of glycerol is small, as is usually the case, the diminution of the increment due to the borax is proportional to the amount of mannitol present, so that if  $p_1$  and  $p_2$  be the amounts deduced respectively from the second and third observations, and  $p$  that subsequently added, the amount originally present in the mother liquor was  $x = pp_1/(p_2 - p_1)$ . This relation is only true, however, when the amount  $p + x$  in the solution is less than 2 per cent. The process of correction may be simplified by means of a table given in the original paper. The specimen results quoted are quite satisfactory.

The solubility of mannitol in alcohol of various strengths and at various temperatures is given in the following table.

Percentage strength of alcohol..	80.0	85.0	90.0
Percentage of mannitol at 3°...	0.556	0.338	0.160
"              "      17°...	0.615	0.351	0.166
"              boiling point....	11.44	6.25	3.62

JN. W.

**Detection of Glucose.** By A. JAWOROWSKI (*Chem. Centr.*, 1894, ii, 537; from *Pharm. Zeit. Russ.*, 33, 487).—Three c.c. of urine is mixed in a test-tube with 0.3 gram of potassium iodate and 0.6 gram of fused sodium hydroxide, the whole boiled for one minute, quickly cooled, and four drops of ammonia added; the tube is then inclined and 20 to 30 drops of dilute hydrochloric acid is slowly added. After this the tube is placed upright and the contents are gently

stirred; where the acid and alkaline solutions meet, a ring is formed. In presence of little glucose, the ring is brownish, darker than the layer of urine below; from the latter it is separated by a colourless, a pale raspberry coloured, or a dirty raspberry coloured layer. The characteristic brown ring disappears after one minute when the amount of sugar is very small, but reappears on gently stirring. If, instead of ammonia, starch paste is used, the mixture becomes blue on adding the acid. Although normal urine behaves in the same way, the author believes that the reaction may serve as the basis of a colorimetric process for estimating sugar in urine.

L. DE K.

**Estimation of Glycuronic acid by its Yield of Furfuraldehyde.** By F. MANN and BERNHARD TOLLENS (*Chem. Centr.*, 1894, ii, 83; from *Zeit. Ver. Rubenzuck-Ind.*, 1894, 426—437).—It has been shown that when glycuronic acid is heated with hydrochloric acid, furfuraldehyde, carbonic anhydride, and water are produced. The carbonic anhydride obtained by distilling glycuronic acid with hydrochloric acid amounted to 26·5 per cent. of the glycuronic acid, whilst that obtained from dextrose or levulose by similar treatment amounted to 1 per cent. The furfuraldehyde which glycuronic anhydride yielded by the same treatment was 15·23 per cent. of the anhydride. Those natural compounds, which readily give glycuronic acid when heated with dilute acids, also yield furfuraldehyde when distilled with hydrochloric acid, and the proportion obtained will be a measure of the glycuronic acid which may be separated from such compounds. Thus euxanthic acid yields 6·16—7·17 per cent. of furfuraldehyde, urochloralic acid 9·88—10·30 per cent., and potassium urobetylchloralate 9·50 per cent.

A. G. B.

**Estimation of Tannins.** By AIMÉ GERARD (*Compt. rend.*, 1895, 120, 358—360).—The method proposed by the author (*Abstr.*, 1882, 1327) of estimating tannins by means of purified sheep-gut employed in the form of violin strings, sometimes fails to give accurate results, but this is due to imperfect purification of the gut which, as purchased, often contains variable quantities of water, fat, and salts soluble in water.

The gut, prepared as carefully as possible, should be obtained in the untwisted form from the makers of violin strings, and purified in the laboratory. It is treated three or four times in the cold with crystallisable benzene in order to extract the fat, and after exposure to air, so that the benzene may evaporate, is washed with water and allowed to dry with free exposure to air at the ordinary temperature, care being taken that the sheets are kept separate during the drying.

C. H. B.

**Sunflower Oil.** By D. HOLDE (*Chem. Centr.*, 1894, ii, 79—80; from *Mitt. Techn. Vers.-A. Berlin*, 1894, 12, 36).—This oil is used for dietetic purposes, and finds application as an adulterant of the more valuable oils which are similarly employed. The addition of sunflower oil to lubricating oils is injurious on account of the drying properties of the oil. From the undecorticated seed, the author

extracted, by means of ether, 26—28 per cent. of a clear yellow oil of agreeable taste; sp. gr. 0.9240 at 15°; iodine absorption, 135; "saponification number," 193; acidity, 5.6 per cent. (as oleic acid) coefficient of expansion, between 20° and 78°, 746—748 (*sic*). The oil is clear at -5°, turbid at -10°, and partly solid at -17°; its viscosity is, on Engler's scale, 8.2 at 20°, 5.5 at 30°, 3.9 at 40°, and 3.1 at 50°. The Bechi test gives no reaction with the oil; the Milliau test gives a yellow colour with a brownish shimmer. In a thin layer, the oil dries solid in five days.

A. G. B.

**Reactions of Chelidonine with Phenols.** By J. A. BATTANDIER (*Compt. rend.*, 1895, **120**, 270—271).—In these experiments, the reagent was mixed with concentrated sulphuric acid, and the alkaloid introduced at the edge of the mixture. Guaiacol gives an intense and persistent crimson colour; thymol, a rose colour slowly becoming purplish; phenol, a rose tint; oil of cloves, a purple colour more intense than the brown produced by the action of the acid on the reagent;  $\alpha$ -naphthol, a dull green;  $\beta$ -naphthol, a brownish colour changing to violet; catechol, a rose colour changing to violet; quinol, yellowish; resorcinol, yellowish, giving place to the blue resulting from the interaction of the two reagents; phloroglucinol, yellowish; pyrogallol, red changing to yellow; gallotannic acid, yellowish, gradually changing to intense green. The ethereal derivatives of the phenols act, as a rule, like the phenols.

The green colour given by a sulphuric acid solution of chelidonine with a trace of nitric acid is produced by other oxidising agents, and is especially brilliant, with a trace of potassium chlorate or an arsenate.

C. H. B.

**Decomposition and Detection of Cocaine in the Animal Body in Cases of Poisoning.** By H. W. GLASENAP (*Chem. Centr.*, 1894, ii, 220).—Cocaine can be detected either as such or as ecgonine after 33 days' exposure to the influence of putrefying flesh or human blood. In cases of poisoning, however, if death has ensued within two hours, it will be found unaltered, but, if more than four hours have elapsed before death, it will be found (in the urine) as ecgonine.

D. A. L.

**Detection of Bile Pigment in Urine.** By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1895, **20**, 460—461; compare *Abstr.*, 1894, ii, 171).—The following method is recommended for separating bile pigment from urine:—50 c.c. of urine, 5 c.c. of a 10 per cent. solution of barium chloride, and 5 c.c. of chloroform are shaken together; the chloroform sinks, and is removed together with a precipitate; the two latter are heated together on the water bath until the chloroform is evaporated and Gmelin's test is then applied to the residue.

W. D. H.

## General and Physical Chemistry.

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**Spectra of Argon and the Aurora Borealis.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, **120**, 662—663).—During the action of the silent discharge on mixtures of argon and benzene vapour (this vol., i, 412) under the particular conditions of the discharge known as “rain of fire,” there is developed an intense, greenish-yellow fluorescence, the spectrum of which shows lines and bands in the yellow, green, blue, and violet very similar to those observed in the spectrum of the aurora borealis. Some of the bands are crossed by black absorption lines, owing to the thickness of the fluorescent layer. The author suggests that the aurora borealis may be due to the production of a fluorescent modification or compound of argon under the influence of atmospheric electricity. C. H. B.

**Argon and its Fluorescence Spectrum.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, **120**, 797—800).—Pure argon, when mixed with benzene vapour, and subjected to the action of the silent discharge, undergoes very little change of volume, and the condensation previously observed (this vol., i, 412) was probably due to the presence of nitrogen as an impurity.

With a coil connected with a Leyden jar, and giving a spark 10—12 mm. in length, the mixture of argon and benzene vapour becomes luminous after a time ranging from 15 minutes to four or five hours. It has a violet tint with a reddish “rain of fire.” After some time the fluorescence becomes much more brilliant, and the colour changes to a brilliant green, and finally to blue. When this point is reached, the fluorescence will continue for several hours, but after a long time, especially if the intensity of the spark is increased, the fluorescence disappears, and only a very feeble luminosity remains. If at an earlier stage the discharge is interrupted, the fluorescence at once disappears, but on again completing the circuit it reappears, either immediately, or after a time increasing with the time that has elapsed since the interruption of the discharge.

The spectrum of the fluorescence consists of a number of bands in the violet and green, and especially in the orange-red. The most distinct are a yellow band, quite distinct from D, of wave-length about 579, crossed by black lines when the discharge has a certain intensity; a green band at about  $\lambda$  547, also crossed by black lines; a brilliant violet band, at about  $\lambda$  438, and another less brilliant, at about  $\lambda$  436. None of these bands coincides with the helium line, nor with the principal line in the spectrum of the aurora borealis. They do, however, correspond with the bright lines of the spectrum of argon at low pressure. The band at 579 corresponds with Crooke's line at 575, and the band at 578 in the aurora spectrum; the green band corresponds with Crooke's group of lines between 555 and 549, and Crooke's line 5557 seems to correspond with the principal line of the aurora spectrum; the violet bands correspond respectively with



Crooke's lines at 433 and 430, and with an important band in the aurora spectrum.

C. H. B.

**Spectra of Selenium and Natural Selenides.** By ARNAUD DE GRAMONT (*Compt. rend.*, 1895, **120**, 778—780).—Selenium in selenides is detected even more easily by the spectroscope than sulphur in sulphides (Abstr., 1894, ii, 434).—The following lines were found to be characteristic of the spark spectra of selenides. The Greek letters are used in the same way as by Salet, and indicate the lines which are most intense in the spectra of selenides as well as in that of pure selenium.

6055.1 very distinct.	δ 5175.8 strong.
5863.4 feeble.	5153.0 very fairly distinct.
5747.0 feeble.	ε 5142.3 strong.
5710.5 distinct.	5106.0 fairly distinct.
5623.2 distinct.	ζ { 5098.0 fairly strong.
5592.8 very distinct.	5094.2 very distinct.
5569.0 fairly distinct.	5068.5 fairly strong.
5524.3 feeble.	5026.0 fairly distinct.
5391.0 very distinct.	η { 4992.0 very distinct.
5373.5 very distinct.	4974.2 very distinct.
α 5303.8 strong.	θ { 4845.2 fairly strong.
β { 5270.3 strong.	4840.4 fairly strong.
5252.1 strong.	μ 4764.6 fairly distinct.
5233.2 feeble.	π 4604.0 very distinct.
γ 5226.2 strong.	4563.0 fairly distinct.
5219.0 very fairly distinct.	4216.0 diffuse.

Several lines seen in the spectrum of pure selenium are more or less masked in the spectra of selenides. The following were observed, and include lines not mentioned by Plücker and Hittorff.

6497.5	6296.0	5440.0	4742.0	4175.0
6478.0	6139.0	5115.5	4401.0	4134.0
6432.0	5697.0	5043.5	4321.0	—

C. H. B.

**Variations in the Rotatory Power of Tartrates.** By P. FREUNDLER (*Ann. Chim. Phys.*, 1894, [7], **3**, 433—524, and 1895, [7], **4**, 235—271).—In this extended work, the author has prepared and studied the properties of 55 derivatives of tartaric acid, in the first instance with the object of testing Guye's law of the product of asymmetry (Abstr., 1893, ii, 204 and 561). If  $a$ ,  $b$ ,  $c$ ,  $d$  are the masses attached to one of the asymmetric carbon atoms, and  $a$  and  $b$  are so selected that their difference is a constant one,

$$(a - b) = m = \text{const.},$$

then the formula for the product of asymmetry simplifies to

$$P = m(c - d) \frac{(a - c)(a - d)(a - c - m)(a - d - m)}{(2a + c + d - m)^6}.$$

This formula is first of all discussed analytically, with the object of determining the number and positions of the changes of sign, and the maxima and minima of rotatory power in each of the series under examination. Applying the results obtained in this way to

the experimental determinations, it is found that the formula furnishes a sufficient approximation in the case of di- and tetra-substituted ethereal salts, when the masses are not equal, and the character of the substituted radicles is not altogether a different one. The author's work affords, therefore, generally a confirmation of GUYE's law of asymmetry.

The author also discusses the question of the influence of organic solvents on the specific rotatory power of some of the ethereal tartrates (compare Abstr., 1893, ii, 562; and 1894, i, 68).

H. C.

**The Measurement of High Temperatures and the Melting Points of some Inorganic Salts.** By JOHN McCRAE (*Ann. Phys. Chem.*, 1895, [2], 55, 95—99).—The author describes a small thermoelectric element which he uses for the determination of temperatures varying from 300° to 1400°. It consists of a junction of platinum and platinorhodium, and the author states that between the above limits the E.M.F. is approximately proportional to the temperature. By its means the following melting points were determined.

Sodium iodide.....	694·7°	Strontium chloride..	853·7°
Potassium iodide....	722·7	Sodium carbonate...	856·7
Potassium bromide..	745·5	Sodium sulphate....	881·2
Sodium bromide....	761·1	Potassium carbonate	887·5
Calcium chloride...	802·1	Barium chloride....	915·6
Potassium chloride..	803·9	Potassium sulphate .	1058·9
Sodium chloride....	811·0		

The boiling point of stannous chloride was found to be 603·25°, whilst the temperatures of an alcohol flame, and the blue point and the hottest part of a Bunsen burner flame were determined as 1488°, 1542°, and 1725° respectively.

L. M. J.

**Thermal Expansions of Aqueous Solutions.** By CARL FORCH (*Ann. Phys. Chem.*, 1895, [2], 55, 100—120).—The thermal expansions of a number of aqueous solutions were determined by the dilatometric method. A noticeable point in the experiments is the construction and employment of a stirrer of iron and platinum inside the bulb of the dilatometer itself, and actuated by rotating magnets. Solutions of the following salts were used. Hydrogen, lithium, sodium, potassium, and ammonium nitrates; hydrogen, lithium, potassium, hydrogen-potassium, zinc, and cupric sulphates; trihydrogen, dihydrogen-potassium, dipotassium hydrogen, and tripotassium phosphates, potassium bromide, potassium iodide, zinc chloride, potassium hydroxide, and sodium hydroxide. The concentrations were in all cases  $\frac{1}{2}$ , 1, and 2 gram equivalents per litre. The results of the experimental determinations are recorded, and tables of the volumes and the coefficients of expansion for every five degrees are added.

L. M. J.

**Relationship between the Latent Heats of Vaporisation and Fusion of Substances belonging to the same Family.** By MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1895, [7], 4, 133—136).—If

$L$  is the latent heat of vaporisation of a substance at the absolute temperature  $T$ , and under the pressure  $p$ , and  $u'$  and  $u$ , the volumes of the gas and liquid respectively,

$$\frac{L}{T} = (u' - u) \frac{dp}{dT}.$$

If  $L$  is the molecular latent heat of vaporisation,  $u'$  will be the same for all substances, and where the molecular volumes of liquid compounds are the same,  $(u' - u)$  will be constant.

If further, as appears to be the case in a large number of instances,  $dp/dT$  is approximately constant,

$$L = \text{const.} \times T,$$

which is the well-known law of Trouton. The author supposes that a similar law would probably hold for the latent heat of fusion. It follows from this that in considering any chemical reaction, the variation of entropy by the simultaneous passage from the liquid to the gaseous state of the two systems compared, will be zero.

H. C.

### Melting Point of the Elements as a Clue to their Genesis.

By CHARLES T. BLANSHARD (*Chem. News*, 1895, **71**, 285—286).—The author points out that with elements of low atomicity and low atomic weight, the melting point varies directly as the atomic weight, whereas in the higher periodic series of elements the melting points are alternately high and low. As this same character is observed in homologous series of carbon compounds, it is inferred that the latter elements may be of higher grade than the former elements.

D. A. L.

**Percussive Ebullition.** By H. WOLPERT (*Zeit. anal. Chem.*, 1895, **34**, 164—165).—The author has not found Beckmann's flask satisfactory (see Abstr., 1894, ii, 268, 444). He places in the neck of the flask a funnel, through which passes a blunt-ended glass rod resting on the bottom of the flask. This arrangement prevents superheating.

M. J. S.

**Relations between the Multiple Proportions of Chemical Compounds and their Heats of Formation.** By MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1895, [7], **4**, 145—213).—The author compares the heats of formation of chemical compounds, related to one another in atomic composition according to the law of multiple proportions, in order to ascertain whether there is any direct relationship between the number of atoms of any particular element present and the heat evolved in the formation of the compound. Hydrogen compounds, halogen compounds, and more especially oxygen compounds, are compared in this way. It appears, in the case of the oxygen compounds, that although heat is, as a rule, developed on the introduction of each additional oxygen atom, the amount of heat evolved decreases as the number of oxygen atoms present increases. The following tables may be quoted in illustration.

*Ethylene, C<sub>2</sub>H<sub>4</sub> (gaseous).*

- + O. Aldehyde, C<sub>2</sub>H<sub>4</sub>O, liquid + 71.7 Cal.
- + 2O. Acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, liquid + 131.8 = 65.9 × 2 Cal.
- + 3O. Glycollic acid, C<sub>2</sub>H<sub>4</sub>O<sub>3</sub>, solid + 174.9 = 58.3 × 3 Cal.
- + 4O. Glyoxylic acid, C<sub>2</sub>H<sub>4</sub>O<sub>4</sub>, solid + 215.7 = 53.9 × 4 Cal.
- + 5O. Oxalic acid, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>O, solid + 277.6 = 55.5 × 5 Cal.

*Propylene, C<sub>3</sub>H<sub>6</sub> (gaseous).*

- + O. Propaldehyde, liquid + 75.7 Cal.
- + 2O. Propionic acid, liquid + 131.9 = 66.0 × 2 Cal.
- + 3O. Lactic acid, liquid + 176.8 = 58.9 × 3 Cal.
- + 4O.
- + 5O. Malonic acid + H<sub>2</sub>O, solid + 282.7 = 56.5 × 5 Cal.
- + 6O. Tartronic acid + H<sub>2</sub>O, solid + 344.2 = 57.4 × 6 Cal.
- + 7O.
- + 8O. Mesoxalic acid + H<sub>2</sub>O, solid + 440.1 = 55.0 × 8 Cal.

H. C.

**Thermochemical Researches on Substitution in Mineral Chemistry.** By MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1895, [7], 4, 433—487).—The author has collected and tabulated a large number of the most recent and exact thermochemical data relative to the heat changes accompanying the replacement of one halogen by another or by cyanogen, oxygen, sulphur, selenium or tellurium, in their metallic compounds, and also for the replacement of one metal by another. The data are given both for the salts in solution and in the anhydrous form. It appears generally that the heat change accompanying the replacement of one electro-negative element by another is independent of the nature of the electro-positive element, when the salts are in solution, but that this does not hold for the same compounds in the anhydrous condition. A similar regularity may be observed in the replacement of one metal by another.

H. C.

**Heat of Formation of Calcium Carbide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1895, 120, 682—684).—The heat of dissolution of calcium carbide in dilute hydrochloric acid with evolution of acetylene and formation of calcium chloride solution is +58.25 Cal. Adopting Berthelot and Matignon's numbers for the heat of formation of acetylene, it follows that

C<sub>2</sub> diamond + Ca solid = C<sub>2</sub>Ca solid... develops -7.25 Cal.

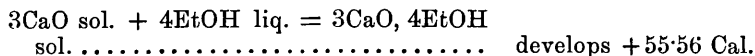
C<sub>2</sub> amorphous + Ca solid = C<sub>2</sub>Ca solid.. „ -0.65 „

If Berthelot's view that acetylene is formed from hydrogen, and gaseous carbon with development of +26.1 Cal., be accepted, the formation of calcium carbide from solid calcium and gaseous carbon develops +76.95 Cal.

C. H. B.

**Compounds of Calcium and Barium Oxides with Alcohol.** By ROBERT DE FORCRAND (*Compt. rend.*, 1895, 120, 737—740).—The compound 3CaO, 4EtOH, previously described (this vol., i, 259), dis-

solves in dilute hydrochloric acid, with liberation of +92.90 Cal., and hence the heat of dissolution in water, which takes place slowly, is +8.90 Cal., and



The value for CaO, +18.52 Cal., is higher than the heat of formation of the hydroxide, +15.10 Cal.

The values for the analogous compound,  $3\text{BaO, 4MeOH}$  (Abstr., 1886, 781) are, heat of dissolution in hydrochloric acid, +112.04 Cal. heat of dissolution in water, +28.94 Cal.; and heat of formation, +63.06 Cal., or +21.02 Cal. for BaO, whereas the heat of formation of the hydroxide is only +17.60 Cal. Moreover, in presence of a small quantity of water the hydrate  $\text{BaO, 2MeOH} + 2\text{H}_2\text{O}$  is formed (Abstr., 1886, 861), with development of +29.74 Cal. from liquid water and +26.88 Cal. from solid water.

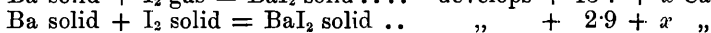
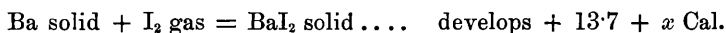
The substance hitherto regarded as barium ethoxide is really a compound analogous to the preceding, and has the composition  $3\text{BaO, 4EtOH}$  (compare Abstr., 1884, 4). Its heat of dissolution in water is +49.07 Cal., and its heat of formation +45.09 Cal., or +15.03 Cal. for BaO, a value 2.57 Cal. lower than the heat of formation of the hydroxide.

These results explain why water decomposes the solution of barium oxide in ethylic alcohol, but not the solution in methylic alcohol.

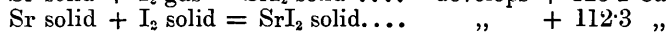
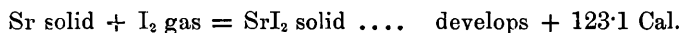
The general result is that the oxides of the calcium group do not form true alkyl oxides, but only additive products, with alcohols of the methyl series.

C. H. B.

**Thermochemistry of Barium and Strontium Iodides.** By TASSILY (*Compt. rend.*, 1895, 120, 733—735).—Crystallised barium and strontium iodides lose hydrogen iodide when heated in nitrogen, but can be obtained anhydrous by heating them in a current of dry hydrogen iodide. The heat of dissolution of barium iodide in water at about 16° is +10.3 Cal., and of strontium iodide at about 12°, +20.5 Cal., and hence



$x$  being the heat of oxidation of barium, and



C. H. B.

**Specific Gravity of Saturated Vapours.** By GUSTAV BAUER (*Ann. Phys. Chem.*, 1895, [2], 55, 184—212).—The specific volume of a vapour may be calculated from Clapeyron's equation,  $r/u = AT(dp/dt)$ , where  $p$  is the pressure in kilos. per sq. cm.;  $u$  the difference between the specific volumes ( $s$  and  $\sigma$ ) of vapour and liquid,  $r$  the heat of vaporisation,  $t$  the temperature,  $T$  the absolute temperature, and  $A$  the equivalent of heat. The results thus obtained have not, however, shown good agreement with those experimentally

obtained. The author has therefore redetermined the specific gravity of the saturated vapours of water, carbon tetrachloride, ether, alcohol, sulphurous anhydride, and chloroform. The method consisted in the accurate weighing of a closed copper vessel (silvered in some experiments) in (1) air and (2) the vapour under examination, necessary corrections for pressure, temperature and expansion of the copper being applied. The experiments with the water vapour were performed at three different localities, namely, Munich, Sonnenblick, and Wendelstein; those with the other liquids were all performed at Munich. The density of the saturated aqueous vapour is found to be very closely represented by the linear function  $\gamma = 0.8101 p$ , the mean difference between these and the observed values being about 0.5 per cent. The values obtained are compared with the observed values of Fairbairn, Wüllner, and Herwig, and with the numbers calculated by Zeuner, Frank, and Fliegner, the best agreement being obtained with the values of the two first observers. Above 600 mm., it is seen that the values depart considerably from those calculated by the use of Regnault's heat of vaporisation. The density referred to air at the same temperature and pressure, is seen to increase with the pressure, being 0.630 at 500 mm. and 0.650 at 760 mm. The determinations with the other liquids gave the following results.

	<i>p</i> .	$\gamma$ .
Carbon tetrachloride .....	712.0 mm.	0.0052
Chloroform .....	725.5 „	0.004248
Ether .....	713.0 „	0.002865
Alcohol.....	717.0 „	0.00149

These values according well with the numbers calculated by Zeuner.  
L. M. J.

**Temperature of Maximum Density of Water.** By L. C. DE COPPET (*Ann. Chim. Phys.*, 1894, [7], 3, 246—268).—If a number of thermometers are so placed in a vessel of water that their bulbs are all in the same horizontal plane, the thermometers themselves being in the same vertical plane, it will be found that on gradually heating or cooling the water, the temperature indicated by each thermometer shows a regular rise or fall for all ranges of temperature except those between 3.5° and 5°. Between 3.5° and 5° the change is an irregular one, so that if for each thermometer a curve is drawn by taking the temperatures as ordinates and times as abscissæ, each curve will be found to cut the others at some point between 3.5° and 5°, this point approximating to the temperature of the maximum density of water.

By taking the mean of a large number of determinations made in this way with both rising and falling temperatures, the author finds the temperature of the maximum density of water to be 4.005°, or 3.982° on the hydrogen thermometer.  
H. C.

**Temperature of Maximum Density and Freezing Points of Cane Sugar Solutions.** By L. C. DE COPPET (*Ann. Chim. Phys.*, 1894, [7], 3, 268—274).—The method adopted by the author for determining the temperature of maximum density of water (preceding

abstract) has been applied to the determination of the temperatures of maximum density of cane sugar solutions.

The results may be expressed by the following empirical formula

$$t_m = 4.01438 - 0.4834P + 0.00082455P^2,$$

where P is the weight of sugar in grams dissolved in 100 grams of water. This formula holds between the limits  $P = 0.344$  and  $P = 11.565$ . The molecular reduction of the temperature of maximum density (compare Abstr., 1893, ii, 60) is calculated, a fairly constant value being obtained.

A comparison of the reduction of the temperature of maximum density D with the reduction of the freezing point C, shows that the ratio D/C has a nearly constant value, and approximates to 8. The values of D/C seem to depend, however, on the concentration, and show a slight regular increase as the concentration rises. H. C.

**Saturated Solutions.** By ALEXANDRE L. ÉTARD (*Ann. Chim. Phys.*, 1894, [7], 3, 275—288).—By the method described in a former paper (Abstr., 1894, ii, 442) the author has determined the solubilities of mixtures of two salts in water at different temperatures. The results are expressed in percentages of the mixed salts, and of each salt taken separately, contained in the saturated solutions, and are also recorded in curve form.

The case of mixtures of sodium and potassium chlorides, which has been given in a previous communication (Abstr., 1890, 103), is first discussed. Mixtures of potassium chloride with potassium bromide and with potassium iodide, and also of potassium bromide with the iodide, were examined. The sum of the salts dissolved is usually represented by a straight line when plotted against the temperature, and the limit of solubility calculated from this, or the point at which, by reason of the increase in the proportion of salt and the decrease in the proportion of water, the latter has disappeared, appears in each case to coincide with the melting point of the lower melting constituent of the mixture. For KCl + KBr this point is at  $703^\circ$ , and the mixture would then contain 25 per cent. KCl and 75 per cent. KBr. For KCl + KI the point is at  $638^\circ$ , the mixture containing 20 per cent. KCl and 80 per cent. KI. For KBr + KI the point is at  $638^\circ$ , the mixture containing 33.3 per cent. KBr and 66.6 per cent. KI.

An attempt was made to measure the solubility of the triple mixture KCl + KBr + KI in water, as a function of the temperature, but it was found that the three salts could not exist simultaneously in a saturated solution, the chloride remaining undissolved in the presence of the other two salts.

The solubility of mixtures of potassium nitrate and sodium chloride was examined more particularly, on account of the interest of the results in connection with the technical preparation of potassium from sodium nitrate.

The following determinations serve to show the general character of the changes in solubility with rising temperature.

Temp.	Per cent. $\text{KNO}_3$ .	Per cent. $\text{NaCl}$ .	$\Sigma$ .
18°	18.9	22.5	41.5
26	20.7	22.3	43.0
35	27.9	20.2	48.1
50	38.5	16.5	55.0
70	49.7	14.0	63.7
90	61.4	10.4	71.8
105	70.0	9.0	79.0
122	73.8	8.0	81.8
145	77.7	7.6	85.3
170	80.7	5.8	86.5

It is evident from these results that in the presence of potassium nitrate, sodium chloride becomes less and less soluble with rising temperature. This fact puts a somewhat different interpretation on the technical process above alluded to than that which is usually given. The limit of solubility appears to lie at 338°, the fusing point of potassium nitrate. Theoretically the solubility of the sodium chloride in the saturated solution would have here fallen to zero, but practically this limit could not be reached, as sodium chloride is soluble in fused potassium nitrate, and this new influence would come into force. Potassium nitrate and potassium chloride when mixed behave towards water at different temperatures just like the mixtures of potassium nitrate and sodium chloride.

Other mixtures examined were those of silver nitrate with potassium nitrate, the limit of solubility being at 198°, the melting point of silver nitrate and the mixture here containing 55 per cent.  $\text{AgNO}_3$  and 45 per cent.  $\text{KNO}_3$ ; of barium nitrate with barium chloride, limit of solubility at 474°, the melting point of barium nitrate, the mixture containing 67.7 per cent.  $\text{Ba}(\text{NO}_3)_2$  and 32.3 per cent.  $\text{BaCl}_2$ ; and of barium bromide with barium iodide. H. C.

**Burner for Monochromatic (Sodium) Light.** By RICHARD PŘIBRAM (*Zeit. anal. Chem.*, 1895, **34**, 166—167).—The lamp, of which a figure is given, affords a brilliant light for long periods. Its essential parts are a wire gauze atmospheric burner, platinum boats containing a mixture of equal parts of sodium chloride and bromide, and a casing with side tubulures and chimney. M. J. S.

**Improvements in Glass Stopcocks.** By H. WOLPERT (*Zeit. anal. Chem.*, 1895, **34**, 161—164).—The author has simplified and improved Winkler's 3-way stopcock by substituting a simple opening into the body of the hollow plug for the bent canal, shortening the plug, lengthening the shell, and narrowing it below the plug to a tube suitable for connection with caoutchouc tubing, thus avoiding the torsion of the caoutchouc tube, which with Winkler's pattern occurred when the plug was turned. M. J. S.

**Simple Percolator.** By RICHARD PŘIBRAM (*Zeit. anal. Chem.*, 1895, **34**, 167—169).—This is a funnel-shaped vessel with a perforated glass shelf near the bottom. Through the shelf passes a narrow



tube, recurved at the top. A glass cover, carrying the condenser, is ground into the top of the funnel. The substance is placed on the perforated shelf, and the percolation is continuous, not intermittent.

M. J. S.

**Safety Valve for Filter Pumps.** By BERLEMONT (*Bull. Soc. Chim.*, 1895, [3], 13, 33—34).—In place of an indiarubber valve, which is objectionable in working with volatile organic liquids, a cylindrical vessel, constricted at the middle, is interposed between the pump and the vessel in which a vacuum is to be maintained, the lower end being connected with the pump, and the upper with the vessel. In the lower chamber there is a glass float, which is ground at the top to fit the constriction, so that if any water regurgitates, the float is carried up, stopping its ingress into the exhausted vessel.

JN. W.

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## Inorganic Chemistry.

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**The Colour, Specific Gravity and Surface Tension of Hydrogen Peroxide.** By WALTER SPRING (*Zeit. anorg. Chem.*, 1895, 8, 424—433).—Pure hydrogen peroxide is prepared by concentrating a 9 per cent. solution on the water bath under diminished pressure until it contains 40—50 per cent.  $\text{H}_2\text{O}_2$ . This solution is treated with ether, the ethereal extract then treated with pure water, and the aqueous solution, after concentration, is again extracted with ether, the ether removed from the extract by distillation, and the residue distilled in a vacuum. The product, which contains 90 per cent.  $\text{H}_2\text{O}_2$ , is fractionally distilled, and the later fractions, which contain no water, are separated.

Pure dry hydrogen peroxide explodes with great violence, and precautions must be taken in distilling it. The specific gravity determined by weighing is 1.4996 at  $15^\circ$ ; a control experiment in which the amount of hydrogen peroxide was determined by titration with permanganate gave sp. gr. = 1.4978. The surface tension was determined by measuring the height to which the liquid rises in a capillary tube, and comparing it with the height to which water rises in the same tube. The number obtained for hydrogen peroxide was 3.5374, and for water 7.750. The surface tension of hydrogen peroxide, however, increases very rapidly when mixed with small quantities of water.

Hydrogen peroxide has a blue colour. A column 1 metre long of 98 per cent. hydrogen peroxide has the same intensity of colour as a column of water 1.8 metres long. With a solution containing 80 grams of hydrogen peroxide to 100 c.c., the intensity of colour compared with that of pure water was found to be 1 : 1.62. The author points out that the ratio of the amounts of condensation of the oxygen atoms in hydrogen peroxide and water is 1.59. Thus the colour, which is characteristic of oxygen and ozone, is also characteristic of water, and, in a higher degree, of hydrogen peroxide. E. C. R.

**Gases of the Helium and Argon Type.** By BOHUSLAV BRAUNER (*Chem. News*, 1895, **71**, 271).—Some time ago the author observed that cerite when treated with sulphuric acid and then with water yielded a gas showing the negative behaviour of nitrogen, but mixed with some hydrogen; the same mineral when heated in a vacuum alone, or with a sulphate, yields gases belonging to the helium and argon type; this was also noticed with several other Bohemian uranium ores. Pitchblende, from Příbram, shows a peculiar behaviour; with a feeble current, in a Geissler tube, with aluminium electrodes, it emits a blue-violet light, with a stronger current, a crimson light. With the spectroscope, the lines,  $D_3$  and  $D_2$  are seen together with 19 other lines or groups of lines; three of the lines belonging to hydrogen and one in the red to argon. After some time the helium lines disappear entirely, one by one, then the hydrogen lines go, and an extremely feeble, but characteristically, fluted hydrocarbon spectrum makes its appearance. The absorption of helium by aluminium proves its metallic character.

D. A. L.

**Helium in Cleveite.** By PER T. CLÈVE (*Compt. rend.*, 1895, **120**, 834).—Cleveite from Carlshuus, Norway, when heated with potassium hydrogen sulphate, yields a gas which, after being passed over red-hot copper and collected over concentrated aqueous potash, shows none of the lines of argon, but contains helium, and gives a spectrum consisting of the following lines: 6677, fairly strong; 5875·9, strong; 5048, fairly strong; 5016, strong; 4922, fairly strong; 4713·5, weaker.

C. H. B.

**Demonstration of the Presence of Argon in the Atmosphere.** By ANTOINE GUNTZ (*Compt. rend.*, 1895, **120**, 777—778).—Magnesium combines somewhat slowly with nitrogen, and requires to be heated to a high temperature, whereas with lithium, prepared by electrolysis (*Abstr.*, 1894, ii, 91), combination takes place readily below a dull red heat.

Nitrogen prepared from the air is enclosed in a glass tube with an iron dish containing lithium, and the latter is gently heated until the pressure in the tube is reduced to 10 mm. A further quantity of nitrogen is allowed to enter, and the heating continued, when it is found that the pressure of the residual gas is about 20 mm. If more nitrogen is admitted the pressure of the residual gas continually increases until at last the tube is practically full of argon. With pure nitrogen, on the contrary, there is no change in the residual pressure, no matter how often gas may be allowed to enter the tube.

C. H. B.

**Free Hydrazine.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1894, **13**, 433—440).—The method of isolating hydroxylamine by acting on the hydrochloride with sodium methoxide is applicable to the isolation of hydrazine, as might be expected, since both the hydrate and its salts are more stable than those of the former base.

The hydrochloride is boiled with a methyl alcoholic solution of the methoxide for half an hour, no heat being evolved as with hydroxylamine, and the product, after removal of the sodium chloride, frac-

tionated under reduced pressure. The tail fraction is then refractionated under ordinary pressure.

On the first attempt, a fraction was obtained containing more hydrazine (73 per cent.) than is present in either the hydrate or its methylic alcohol analogue,  $\text{N}_2\text{H}_4\cdot\text{MeOH}$ . Free hydrazine was therefore present. In a second experiment, a fraction was obtained containing 82–84 per cent. of hydrazine, and boiling at  $63\text{--}64^\circ$  (110–111 mm.), and this, after fractional crystallisation, yielded crystals melting at  $-1^\circ$  to  $-2^\circ$ , and containing 92 per cent. of free hydrazine. The hydrate melts below  $-40^\circ$ .

The base thus obtained is extraordinarily hygroscopic, a fact sufficient to account for the low result of the analysis. It burns quietly, and, unlike hydroxylamine, does not explode on heating. When spread over a large surface, it oxidises quickly with evolution of heat, but it oxidises only slowly in mass. It is heavier than water, with which, as stated above, it combines with great avidity, and evolution of much heat. It dissolves sulphur crystals with evolution of heat to a reddish-brown liquid, having an odour resembling that of ammonium sulphide, from which sulphur is precipitated by water. The halogens combine violently with the base to form the free halogen acids; iodine, for example, oxidises it to nitrogen, being itself reduced to hydrogen iodide. The hypothetical diimide,  $\text{NH}\cdot\text{NH}$ , is not apparently, formed, but this point is being investigated. The base is oxidised violently by solid potassium permanganate and dichromate, but the action is not so violent as with hydroxylamine, no ignition or explosion occurring. It dissolves various salts, potassium chloride, bromide, and nitrate, for instance. JN. W.

**Action of Hydrogen on Amorphous Phosphorus.** By HERBERT McLEOD (*Chem. News*, 1895, **71**, 245), and by GEORGE YOUNG (*ibid.*, 281).—McLeod has not recognised any action when hydrogen is passed over or left in contact with heated amorphous phosphorus. In the former case the escaping gas after passing through a water wash-bottle, fumed in air, but was not spontaneously inflammable, and after passage through a U-tube filled with wet glass beads, it neither fumed nor formed any copper phosphide in a solution of copper sulphate.

Young observed, in similar experiments, that with a rapid current of hydrogen and with the wash-bottle omitted, the issuing gas became inflammable, but that it was deprived of this property by passing it through a glass spiral, kept cool by water, just as readily as by the wash-bottle. D. A. L.

**Reduction of Carbonic Anhydride at Ordinary Temperatures.** By ADOLF LIEBEN (*Monatsh.*, 1895, **16**, 211–247).—According to Maly (*Annalen*, **135**, 118), carbonic anhydride is reduced to formic acid when treated with nascent hydrogen in the presence of a strong base. In this paper, a number of experiments are described which were undertaken with the object of confirming and extending Maly's work.

The author finds that when portions of sodium amalgam are added

to water, through which a slow stream of carbonic anhydride is kept passing for several weeks, a considerable quantity of sodium formate, but of no other reduction product, is obtained.

Potassium and barium amalgam react in a similar manner, and the reduction appears to be independent of sunlight. Sodium amalgam also reduces carbonic anhydride in alcoholic solution, but the amount of sodium formate obtained is considerably less than when the aqueous solution is used. Small quantities of formic acid are also produced when the sodium amalgam reacts in the presence of mineral acids such as phosphoric and sulphuric. The amount of formic acid thus obtained appears to diminish with the amount of mineral acid which is present.

Zinc and aluminium in the presence of mineral acids have no appreciable reducing action on carbonic anhydride. Aluminium amalgam does not reduce an aqueous solution of the anhydride, but in the presence of alkaline salts, such as sodium hydrogen carbonate, sodium phosphate, potassium sulphate, and potassium tartrate, small quantities of formic acid are produced. When magnesium or platinised magnesium reacts on an aqueous solution of carbonic anhydride, no formic acid is obtained even in the presence of alkali salts. Platinised zinc also has no reducing action on an aqueous solution of the anhydride to which potassium or ammonium hydroxide has been added.

The author is unable to confirm Maly's statement that formic acid is produced when hot potassium hydroxide reacts with zinc and zinc carbonate. The author thinks his results may be summarised as follows.

1. Aqueous solutions of carbonic anhydride are not reduced by nascent hydrogen at the ordinary temperature.
2. Bicarbonates of the alkali or alkaline-earth metals (with the exception of magnesium), especially when freshly formed, are readily reduced by nascent hydrogen to the corresponding formates.
3. Formic acid is the only product of reduction, and sunlight plays no part in the process.

J. J. S.

**Sodium Hydrogen Sulphite.** By REGINALD E. EVANS and CECIL H. DESCH (*Chem. News*, 1895, **71**, 248).—During the severe cold of last winter, a solution of sodium hydrogen sulphite, sp. gr. 1.290, deposited crystals of the composition  $\text{Na}_2\text{S}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , which tended to effloresce in the air, and had a faint odour of sulphurous anhydride. In warmer weather these crystals deliquesced and formed pearly white crystals of sodium pyrosulphite,  $\text{Na}_2\text{S}_2\text{O}_5$ , suspended in a solution of sodium hydrogen sulphite, sp. gr. 1.165.

D. A. L.

**Sodium Thiosulphate in Photography.** By ALPHONSE SEYEWETZ and G. CHICANDARD (*Bull. Soc. Chim.*, 1895, [3], **13**, 11—18).—A study of the conditions which render photographs fixed by thiosulphate fugitive.

The fading is probably due to the action of products arising from the action, on the one hand, of mineral acids, and on the other hand, of alum, on the excess of thiosulphate. With excess of acid, the

thiosulphate is decomposed in the well-known manner, but with excess of thiosulphate, secondary actions take place, resulting in the liberation of hydrogen sulphide; sodium sulphate and sulphite also appear to be formed. With alum, the effect is much the same.

JN. W.

**Compounds of Lithium Bromide and Chloride with  $3\text{H}_2\text{O}$ .** By A. BOGORODSKI (*Chem. Centr.*, 1894, ii, 514; from *J. Russ. Chem. Soc.*, **26**, 209).—Crystals of  $\text{LiBr} \cdot 3\text{H}_2\text{O}$  can be obtained by cooling to  $-40^\circ$  a solution having the composition  $\text{LiBr} + 4\text{H}_2\text{O}$ ; they decompose at  $4^\circ$ ,  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  being formed. Crystals of  $\text{LiCl} \cdot 3\text{H}_2\text{O}$  can be obtained from a solution having the composition  $\text{LiCl} + 3 \cdot 3\text{H}_2\text{O}$ , when it is cooled to  $-25^\circ$ ; they decompose at  $-15^\circ$ . The temperatures at which the various hydrates decompose are:—

	$3\text{H}_2\text{O}$ .	$2\text{H}_2\text{O}$ .	$1\text{H}_2\text{O}$ .
$\text{LiCl} \dots\dots$	$-15^\circ$	$12 \cdot 5^\circ$	$98^\circ$
$\text{LiBr} \dots\dots$	4	$44 \cdot 0$	159 (not $115^\circ$ )
$\text{LiI} \dots\dots$	72	$80 \cdot 0$	300

C. F. B.

**Double compound of Lithium and Lead Iodides.** By A. BOGORODSKI (*Chem. Centr.*, 1894, ii, 515; from *J. Russ. Chem. Soc.*, **26**, 216).—Small portions of lead iodide are introduced into a solution of lithium iodide, kept constantly stirred, at  $140$ – $150^\circ$ , until yellow flakes begin to separate; water is then added until the precipitate formed is just permanent, the excess of water is evaporated, and the solution, now become clear again, is set aside. Yellow needles of  $\text{PbI}_2 \cdot \text{LiI} + 5\text{H}_2\text{O}$  crystallise out; they should be pressed at a temperature above  $72^\circ$ , otherwise they may become contaminated with  $\text{LiI} \cdot 3\text{H}_2\text{O}$ . At  $95^\circ$  they lose  $1\text{H}_2\text{O}$  and turn red; the other  $4\text{H}_2\text{O}$  is lost only after long drying at  $100^\circ$ . In the air they take up  $1\text{H}_2\text{O}$ , and turn red; the crystals thus formed become yellow again at  $88^\circ$ .

C. F. B.

**Solubility of Anhydrous Calcium Sulphate.** By ALEXEI L. POTILIZIN (*Chem. Centr.*, 1894, ii, 515; from *J. Russ. Chem. Soc.*, **26**, 170).—The solubility was determined by drying a weighed quantity of calcium sulphate for a given time at a given temperature, shaking it for a given time with a measured quantity of water, filtering, and evaporating a weighed quantity of the solution. The solubility varies (1) with the temperature and time of the drying; (2) to a certain extent, with the relative amount of the salt; and (3) with the time of shaking. In experiments with 1–2 grams of substance, the solubility is constant when the drying is done at temperatures between  $96^\circ$  and  $200^\circ$ ; as the temperature of drying rises above  $200^\circ$ , the solubility decreases. With samples dried at the same temperature, the solubility increases somewhat when a larger quantity of the salt is taken, and a similar, but smaller, effect is produced when the salt is dried for a longer time. After a certain limit in the time of shaking, the solubility decreases; this is because hydrated salt separates out from the solution. These results are explained by supposing that there are two kinds of anhydrous calcium sulphate;  $\alpha$ , which is formed between  $120^\circ$  and  $200^\circ$ , readily takes up  $2\text{H}_2\text{O}$ , and

“sets” with water (plaster of Paris);  $\beta$ , which is ignited gypsum, or anhydrite, takes up water with difficulty and does not set. As a rule, mixtures of the two are obtained; but the lower the temperature and the shorter the time of drying, the less of the  $\beta$  variety is formed.

C. F. B.

**Magnesium Fluorides and Silicates.** By ANDRÉ DUBOIN (*Compt. rend.*, 1895, **120**, 678—681).—When dry magnesia is added in successive small quantities to potassium fluoride, fused at a bright red heat, it gradually dissolves, and if the mass is allowed to cool slowly, and is treated with water, the double fluoride,  $\text{MgF}_2 \cdot 2\text{KF}$ , is obtained in flattened, quadratic prisms. The same product is obtained by the action of potassium hydrofluoride on magnesia, and is attacked by both sulphuric and hydrochloric acids; sp. gr. at  $0^\circ = 2.8$ .

When magnesia is added in somewhat large quantity, another product,  $\text{MgF}_2 \cdot 2\text{KF}$ , is obtained in addition to the preceding compound. Its sp. gr. at  $0^\circ$  is 2.7, and it is attacked by sulphuric and hydrochloric acids.

Analogous and well crystallised products in which the fluorine is partially replaced by chlorine are obtained by fusing the preceding crude products with potassium chloride.

No silicate is obtained by adding silica to the fused potassium fluoride containing magnesia, even when the product is afterwards fused with potassium chloride. If, however, one part of magnesia and 4 parts of silica are dissolved in fused potassium fluoride and the product is afterwards fused with potassium chloride and kept at a red heat for about three days, the compound,  $\text{MgO} \cdot \text{K}_2\text{O} \cdot 3\text{SiO}_2$ , is obtained in hexagonal crystals, with a negative axis, and flattened parallel with the base. Its sp. gr. at  $0^\circ$  is 2.55, and it is readily attacked by acids. Another silicate containing both chlorine and fluorine is produced at the same time in highly birefractive flattened crystals with rectangular forms which show longitudinal extinction.

C. H. B.

**Alloys of definite Composition.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1895, **120**, 835—837).—The alloy,  $\text{SnCu}_3$ , is obtained in white, crystalline lamellæ, by fusing copper with an excess of tin and treating the product with cold concentrated hydrochloric acid. It is not attacked by acids, and is one of the definite compounds indicated by the physical researches of several previous observers.

The compound,  $\text{Zn}_2\text{Cu}$ , is obtained by fusing copper with excess of zinc, and treating the product with very dilute hydrochloric acid or, better, a paste of lead chloride. It forms small, white needles, and its composition agrees with that deduced by Laurie from his observations on electromotive forces.

The compound,  $\text{AlCu}$ , is obtained in like manner; the crude product being treated with very dilute hydrochloric acid, or very dilute potash solution. It forms white crystals, which acquire a bronze colour if subjected too long to the action of the acid or alkali.

A zinc chromium alloy is obtained in hexagonal lamellæ by fusing a mixture of chromic chloride and alkali chlorides with excess of zinc

and treating the product with dilute hydrochloric acid, or better a paste of lead chloride.

All these alloys are hard and brittle.

C. H. B.

**Cerite Metals.** By PAUL SCHÜTZENBERGER (*Compt. rend.*, 1895, **120**, 663—668).—Purified cerium sulphate prepared from cerite was converted into the oxalate and then into the nitrate, and the latter was fused with potassium nitrate according to Debray's method. The yellow oxide thus obtained was again converted successively into sulphate, oxalate, and nitrate, and the latter was again fused with potassium nitrate. Cerium oxide prepared in this way is almost white and is quite free from didymium. It was then converted into ceric sulphate by the action of concentrated sulphuric acid, and this was changed into the cerous salt by heating at dull redness. After purification by repeated crystallisations from water, the cerous salt was heated at  $440^{\circ}$  in a current of dry air.

The sulphuric acid in cerous sulphate cannot be accurately estimated by precipitation with barium chloride in presence of hydrochloric acid. If, however, a hot solution is precipitated with pure sodium hydroxide, filtered, and the filtrate acidified with hydrochloric acid, and precipitated with a *very slight* excess of barium chloride, the barium sulphate obtained is pure. The small quantity of sulphuric acid precipitated with the cerous oxide is removed by redissolving the latter in hydrochloric acid, again precipitating with alkali, and treating the filtrate with hydrochloric acid and barium chloride.

Analyses of cerous sulphate made in this way gave 139.45 for the atomic weight of cerium.

Brauner's method of converting the sulphate into oxide by strongly heating, gave results that varied with the temperature. The values obtained by the synthesis of cerous sulphate from the oxide were also unsatisfactory and varied from 139 to 143 according to the temperature at which the oxide had previously been heated.

Direct experiment showed that cerium dioxide is slightly oxidised by the air.

The cerium dioxide obtained by two or three successive fusions with potassium nitrate is free from lanthanum and didymium, but if it is converted into cerous sulphate and the latter is subjected to fractional crystallisation, the atomic weight of cerium obtained by converting the cerous sulphate into oxide by strongly heating, gradually decreases with successive fractions. In the examples quoted the decrease is from 139.4 to 135.2, and it is clear that the cerium dioxide obtained by Debray's method must contain metals other than cerium.

C. H. B.

**Cerium.** By BOHUSLAV BRAUNER (*Chem. News*, 1895, **71**, 283—285).—The author points out that he sometime ago discovered the compound character of ordinary cerium, mentioned by Schützenberger (preceding abstract), and is still investigating cerium. He confirms Mendeléeff's view as to the composition of the sulphate,  $\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{Ce}_2\text{O}_4 \cdot 4\text{SO}_3 + 24\text{H}_2\text{O}$ , from the results of analysis and synthesis, as well as from the fact that similar salts may be prepared, in which



other trivalent earth-metals replace the trivalent cerium, such for example as  $\text{La}_2\text{O}_3, 3\text{SO}_3 + \text{Ce}_2\text{O}_3, 4\text{SO}_3 + 24\text{H}_2\text{O}$ .

Ceric hydroxide exists in two modifications, one insoluble in cold hydrochloric acid, the other soluble giving a brownish-yellow solution of the tetrachloride which decomposes with the evolution of chlorine, even at  $-18^\circ$ .

Cerium can be more or less completely split up into its constituents by various means. Fractionating ceric oxide by solution in sulphuric acid results in a residue insoluble in boiling concentrated sulphuric acid which can be dissolved by fusion with potassium hydrogen sulphate, or by boiling with hydrochloric acid and potassium iodide; the oxalate of this leaves on ignition a rose-brown (dark salmon-coloured) oxide of an element called by the author "*meta-cerium*." Other means employed were partial reduction of ceric oxide in hydrogen and extraction of the products; fractional precipitation with oxalic acid; fractional crystallisation of the sulphate and precipitation of the mother liquor by alcohol; fractional crystallisation of ceric ammonium nitrate; fractional crystallisation of cerous ammonium nitrate, Mendeléeff's method; accumulating the new earth in the mother liquors from the precipitation of cerium as basic nitrate or sulphate, and obtaining it from them by combining Debray's method with one of the above methods. In the spark spectra of different fractions of cerium some lines are common to cerium and meta-cerium, whilst other lines are characteristic for each of them.

A re-determination of the atomic weight of cerium has been made, based on the analysis of the normal oxalate by Gibbs' method, using *old* potassium permanganate of an invariable standard and carefully ascertaining and correcting for the active oxygen contained in the ceric oxide over and above  $\text{Ce}_2\text{O}_3$ ; as a result the numbers 139.91, 139.72 and 140.01 have been obtained, of which the author prefers the last.

The oxidation of colourless cerous to yellow ceric salts by means of permanganate,  $3\text{Ce}_2\text{O}_3 + 2\text{KMnO}_4 + \text{H}_2\text{O} + \text{Aq} = 2\text{KHO} + 2\text{MnO}_2 + 3\text{Ce}_2\text{O}_4 + \text{Aq}$ , is used by the author for the volumetric estimation of cerium, the excess of permanganate is estimated in the filtrate after the removal of the hydrated oxides. In acid solutions, the yellow ceric colour interferes with the perception of the end reaction, but in alkaline solution excellent results are obtained and the method is invaluable for determining trivalent cerium in the presence of tetravalent cerium and of cerium in any form (tetravalent may first be reduced by sulphurous acid) in the presence of other non-oxidisable earths.

The communication concludes with some comments on the position of the rare earth elements in the periodic system and the note that "the valency of the rare earth elements increases with increasing atomic weight."

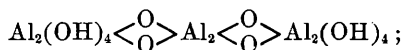
D. A. L.

**Aluminium Compounds.** By ERNEST SCHLUMBERGER (*Bull. Soc. Chim.*, 1895, [3], 13, 41–65).—The precipitate formed when aluminium sulphate is exactly neutralised with alkali consists of a *basic sulphate* having the composition  $2\text{Al}_2\text{O}_3, \text{SO}_3, 7\text{H}_2\text{O}$ , and the probable constitution,  $[\text{Al}_2(\text{OH})_5]_2\text{SO}_4, 2\text{H}_2\text{O}$ . It is stable only in presence of

alkali sulphates, and is partially dissolved by water. The dry substance loses  $2\text{H}_2\text{O}$  at  $130^\circ$ , but is otherwise stable. It is soluble in cold acetic acid, but is reprecipitated on boiling, and redissolves on cooling, in this resembling the ordinary aluminium mordanting solution, the essential constituent of which appears to be an acetate of this sulphate. The same sulphate is precipitated when sodium aluminate is neutralised with alum, or when a solution of alum, to which alkali has been added until a slight permanent precipitate is formed, is boiled, or when a solution of aluminium acetate is boiled with alkali sulphates.

An analogous *basic carbonate*,  $[\text{Al}_2(\text{OH})_5]_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , is precipitated by large excess of sodium carbonate from aluminium salts of monobasic acids, or by carbonic anhydride from cold solutions of alkali aluminates. The composition of the salt varies with the basicity of the acid, a fact which explains the discordant results obtained by previous authors.

Various hydroxides were prepared. The normal hydroxide,  $\text{Al}(\text{OH})_3$ , could not be obtained in a pure condition, as on removal of the alkali salts, it lost, to a large extent, its solubility in acids. The product thus obtained was in fact, a mixture of a soluble, probably normal hydroxide, and an insoluble, colloidal form. These may be separated by means of dilute hydrochloric acid or alkali, and the latter form may be readily prepared by boiling aluminium salts with large excess of alkali. The ordinary hydroxide precipitated in estimating alumina usually contains a large amount of the colloidal hydroxide, especially if the solution has been boiled to expel ammonia; this is objectionable, as the colloïd tends to become gelatinous, or even soluble, after the removal of the alkali salts. The composition of these hydroxides is not particularly definite. The chief is *metatrialuminium hydroxide*,  $\text{Al}_6\text{O}_{14}\text{H}_{10}$ , possibly



this forms white, translucent clots, and is very hygroscopic. It swells up in cold, concentrated mineral acids, but does not dissolve readily until heated, when it forms normal aluminium salts. On the other hand, it dissolves with great ease in cold, dilute hydrochloric acid to a viscous, opalescent, but homogeneous liquid, which passes through filter paper. This liquid, which is acid and astringent, appears to coagulate when concentrated, and the dried coagulum forms a gummy mass of the composition,  $\text{Al}_6\text{O}_{14}\text{H}_{10} \cdot \text{HCl}$ . When the solution of this *hydrochloride* is dialysed, normal aluminium chloride is eliminated, and the original basic hydroxide remains. A corresponding *nitrate*, and *acetate* were prepared, and a *sulphate* appears to exist. Other hydroxides were prepared containing a larger percentage of the base, but probably of the same type. The colloidal hydroxides do not appear to act as mordants, and it is probable that the deteriorating effect of alkalis or even steam on the mordanting power of alumina is due to their formation.

JN. W.

**Properties of Nickel and Cobalt Salts.** By LUCIEN L. DE KONINCK (*Compt. rend.*, 1895, **120**, 735—737).—The author claims priority for himself, Lecrenier, and Ledent, with regard to a detailed description (*Traité de Chimie analytique minérale*, Liege, 1894) of the behaviour of nickel and cobalt sulphides with alkali sulphides. (See Villiers, this vol., ii, 228—247.) C. H. B.

**Dichromates of the Heavy Metals.** By GERHARD KRÜSS and OSKAR UNGER (*Zeit. anorg. Chem.*, 1895, **8**, 452—463).—The dichromates of the heavy metals cannot be obtained in a crystalline form, except a lead dichromate described by Preis and Rayman (*Ber.*, 1880, **13**, 340), which is obtained by dissolving lead chromate in hot concentrated chromic acid, and crystallises in small, interlacing needles, and a copper dichromate  $\text{CuCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , which separates in undefined crystals, and has been described by Freese (*Ann. Phys. Chem.*, **140**, 87) and Balbiano (*Gazzetta*, **18**, 195).

The crystalline double salts of dichromates of the heavy metals and alkalis described below, are only obtained under special conditions, and decompose into their components when recrystallised.

**Cobalt ammonium dichromate**,  $\text{CoCr}_2\text{O}_7 \cdot (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O}$ , is obtained by dissolving molecular proportions of ammonium dichromate and cobalt nitrate in the smallest possible quantity of hot water, and allowing the solution to cool slowly. After the first crystallisation has taken place, the viscid mother liquor is allowed to remain in a vacuum for three weeks when the salt separates in black, lustrous plates. It is very slightly hygroscopic, dissolves in water with difficulty, and loses its water of crystallisation completely at  $105^\circ$ .

**Cadmium potassium dichromate**,  $\text{CdCr}_2\text{O}_7 \cdot \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O}$ , is obtained by dissolving the precipitate of basic chromate, prepared from potassium chromate and cadmium nitrate in chromic acid, and then concentrating the solution on the water bath. It crystallises in bright, brownish-red, four-sided prisms, is slightly hygroscopic, and gives up its water of crystallisation and darkens at  $105^\circ$ .

**Copper ammonium dichromate**,  $2\text{CuCr}_2\text{O}_7 \cdot 3(\text{NH}_4)_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{O}$ , is easily obtained by adding copper dichromate to a hot concentrated solution of ammonium dichromate. It crystallises in long, dark brown needles, loses its water of crystallisation, and is decomposed at  $100^\circ$ , and burns violently with evolution of flame and formation of chromic oxide.

When a concentrated solution of a dichromate of a heavy metal, prepared by dissolving the hydroxide in concentrated chromic acid, is mixed with a hot solution of mercuric chloride, and the mixture allowed to cool, most of the mercuric chloride separates unchanged. The mother liquor, which still contains mercury when evaporated to a syrup, partially crystallises in long, colourless needles. If, however, mercury cyanide is employed in place of the chloride well characterised double salts are obtained.

Silver dichromate mercury cyanide,  $\text{Ag}_2\text{Cr}_2\text{O}_7 \cdot \text{Hg}(\text{CN})_2$ , has already been described by Darby (*Annalen*, 1848, **65**, 205), who prepared it by adding silver nitrate to the salt  $3\text{Hg}(\text{CN})_2 \cdot 2\text{K}_2\text{CrO}_4$ . It is

most easily obtained by adding a solution of potassium dichromate to a hot solution of silver nitrate and mercury cyanide until a faint, permanent precipitate is formed. It crystallises in slender, radiating prisms, having a beautiful, golden-red colour and a characteristic iridescence. When heated, it explodes violently, with the formation of chromic oxide, and metallic silver and mercury. The authors were unable to obtain the corresponding thallium salt.

The following double salts are not so easily obtained, as the chromic acid decomposes the mercury cyanide, even at the ordinary temperature. The best results are obtained by avoiding an excess of chromic acid, and concentrating the solutions at  $45^{\circ}$  in a current of dry air. The salts are easily recrystallised, and when pure can be boiled with water without decomposition.

*Cobalt dichromate mercury cyanide*,  $\text{CoCr}_2\text{O}_7 \cdot 2\text{Hg}(\text{CN})_2 + 7\text{H}_2\text{O}$ , is obtained by mixing hot concentrated solutions of cobalt nitrate, ammonium dichromate, and mercury cyanide. It crystallises in brownish-red, transparent tablets having a diamond lustre. When exposed to the air, it gradually gives up its water of crystallisation. The anhydrous salt is dark brownish-red. When heated at  $300^{\circ}$ , it explodes violently, with the formation of a thick cloud of cobalt and chromium oxides and deposition of mercury.

*Nickel dichromate mercury cyanide*, prepared in a similar manner, crystallises with  $7\text{H}_2\text{O}$  in dirty green concretions.

*Cadmium dichromate mercury cyanide* is obtained by carefully evaporating a solution of cadmium dichromate and mercury cyanide. It crystallises with  $7\text{H}_2\text{O}$  in red, lustrous tablets, is not hygroscopic, detonates on heating, and resembles the cobalt salt.

*Zinc dichromate mercury cyanide*, prepared in a similar manner to the preceding salt, crystallises with  $7\text{H}_2\text{O}$  in large, rhombic red tablets, gives up its water of crystallisation and decomposes at  $100^{\circ}$ , and detonates at a higher temperature.

*Copper dichromate mercury cyanide*,  $\text{CuCr}_2\text{O}_7 \cdot \text{Hg}(\text{CN})_2 + 5\text{H}_2\text{O}$ , is obtained in a similar manner to the above salts; the yield, however, is very small. It separates in greenish-brown nodules, is easily soluble in water, and decomposes at  $100^{\circ}$ .

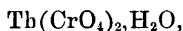
E. C. R.

**Atomic Weight of Molybdenum.** By KARL SEUBERT and WILLIAM POLLARD (*Zeit. anorg. Chem.*, 1895, 8, 434—451).—The method is based on the acidimetric determination of molybdic acid, previously described by the author (this vol., ii, 331). The molybdic acid is purified as follows:—It is dissolved in ammonia, and the solution evaporated to dryness with the addition of a few drops of ammonium sulphide. The residue is taken up with water and ammonia, filtered, and the filtrate crystallised. After two recrystallisations, the salt is decomposed with excess of nitric acid, and evaporated to dryness. The molybdic acid is then washed with water, strongly heated in a platinum dish, and finally sublimed in a current of oxygen. A weighed quantity of the molybdic acid, previously heated at  $110^{\circ}$ , is dissolved in a weighed quantity of standard sodium hydroxide solution, a slight excess being employed, and heated on the water bath until it is completely dissolved. Phenolphthalein

is then added, and a slight excess of standard sulphuric acid, and the solution boiled for 10 minutes to expel carbonic anhydride. The excess of acid in the cold solution is then determined by the addition of standard lime water. At the same time the sulphuric acid is titrated against the lime water, and a blank experiment is performed. The mean of 11 experiments gave  $\text{Mo} = 95.722$  when  $\text{H} = 1$ , or when the weights are corrected to vacuum  $\text{Mo} = 95.729$ .

As a control on the above method the authors have also determined the atomic weight by the reduction of molybdic acid to molybdenum in a current of pure hydrogen. A weighed quantity of the acid in a platinum boat is heated cautiously in a current of hydrogen until it is converted into the dioxide. The temperature is then gradually increased to a bright yellow, and finally the resulting molybdenum is allowed to cool in a current of hydrogen and weighed. The mean of five experiments gave  $\text{Mo} = 95.772$ , or when corrected to vacuum  $\text{Mo} = 95.735$  ( $\text{O} = 15.96$ ).  
E. C. R.

**Chromates of the Rare Earths. Chromates of Thorium.** By CHASE PALMER (*Amer. Chem. J.*, 1895, **17**, 374—379).—When thorium hydroxide is gradually added to a solution of pure chromic anhydride in water, the hydroxide is dissolved but *thorium chromate*,



soon separates, first as a flocculent and then a crystalline, orange precipitate. The precipitate forms more quickly at  $90^\circ$ , and only loses its water of crystallisation at  $180^\circ$ . If the solution is evaporated over sulphuric acid in a vacuum, the salt crystallises with  $3\text{H}_2\text{O}$  in orange scales. These lose  $2\text{H}_2\text{O}$  at  $120^\circ$ , and the third molecule only at  $180^\circ$ . The salt is also precipitated (immediately in hot solutions, slowly in cold) when thorium nitrate and potassium dichromate are mixed. If thorium nitrate (1 mol.) is treated with potassium chromate, a *basic chromate*,  $\text{Th}(\text{OH})_2\text{CrO}_4$ , separates as a golden-yellow precipitate, the solution becoming red from formation of potassium dichromate. If this precipitate is left in contact with the solution, it is gradually changed into the orange normal salt, with reconversion of the solution into yellow potassium chromate. Thorium chromate is readily soluble in hydrochloric acid and in ammonium carbonate, and at  $22^\circ$  one part is soluble in 284 parts of water. The anhydrous salt is of an ochreous-yellow colour, and decomposes at a dull red heat.

The author is now investigating the chromates of zirconium, of which he has obtained a basic salt.  
L. T. T.

**Platinous Chloride and its Compounds.** By LÉON PIGEON (*Compt. rend.*, 1895, **120**, 681—682).—Chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , is exactly neutralised with barium carbonate, and the solution is mixed with barium dithionate in exactly molecular proportion, previously dissolved in three times its weight of water, and the mixture is heated on a water bath for 24 hours. Platinous chloride, hydrochloric acid, and barium sulphate are formed, and the filtered liquid contains only the first two products. Since platinous chloride will not crystallise, it is

best converted into the double potassium compound by addition of potassium chloride, and any traces of platonic chloride remaining unreduced are of course precipitated.

C. H. B.

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## Mineralogical Chemistry.

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**Aluminosilicates.** By STANISLAUS J. THUGUTT (*Jahrb. f. Min.*, 1895, *Beil. Band*, 9, 554—624; compare Abstr., 1893, ii, 421).—Numerous experiments were made on various aluminous silicates, which show that the aluminium plays different rôles in the molecule; attempts were also made to arrive at the constitution of the minerals treated. The experiments consisted in the prolonged digestion of the material with dilute solutions (usually 1—2 per cent. potassium carbonate) at temperatures of about 200°.

The artificial natronnepheline hydrate,  $4\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ , on such digestion, splits up into a potassiumnatrolite,  $\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , and sodium aluminate,  $\text{Na}_2\text{Al}_2\text{O}_4$ ; its constitution is, therefore, represented as  $4(2\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}, \text{Na}_2\text{Al}_2\text{O}_4), 15\text{H}_2\text{O}$ ; by digestion with pure water, natrolite and kaolin are obtained. On fusing the last material, soda-anorthite (natronanorthit,  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_8$ ), is obtained; this gives the same results on digestion as before, and a similar constitution is given. Artificial kaliophilite (kalinephelin,  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8 = 2\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}, \text{K}_2\text{Al}_2\text{O}_4$ ), is converted by the same treatment into a potash mica and free potash: as potash mica has the same empirical formula as this substance, it is probably also of the same constitution, namely,  $\text{K}_2\text{H}_2\text{Al}_4\text{Si}_6\text{O}_{20}, \text{H}_2\text{Al}_2\text{O}_4 [= (\text{K}, \text{H})_2\text{Al}_2\text{Si}_2\text{O}_8]$ , this agrees with the more basic potash-micas, whilst in the more acid (Tschermak's phengite) the group  $\text{H}_2\text{Al}_2\text{O}_4$  is omitted.

According to Lemberg the members of the sodalite group correspond with natronnepheline hydrate in having a sodium salt in place of water; this is confirmed by the action of the potassium carbonate solution being the same in both. The constitution of sodalite is given as  $8\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}, 4\text{Na}_2\text{Al}_2\text{O}_4, 8\text{NaCl}$ . The action of pure water on sodalite gives rise to natrolite, sodium aluminate, sodium chloride, and some kaolin; from these various products, sodalite can be reconstructed. Owing to the somewhat different behaviour of artificial and various natural specimens of sodalite, when digested with calcium chloride solution, three metameric varieties of this mineral are distinguished. The reactions with nepheline are much the same as those of sodalite, and the similar constitutional formula  $8\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}, 4\text{Na}_2\text{Al}_2\text{O}_4, 3\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}$  is deduced. Kaolin, with dilute caustic potash solution, gives potassium natrolite and potassium aluminate; hence its formula,  $2\text{H}_2\text{Al}_2\text{Si}_3\text{O}_{10}, \text{H}_2\text{Al}_2\text{O}_4, 3\text{H}_2\text{O}$ . Sanidine, on the same grounds, is given as  $2\text{K}_2\text{Al}_4\text{Si}_3\text{O}_{10}, \text{K}_2\text{Al}_2\text{O}_4, 12\text{SiO}_2$ .

The constitutions of natrolite, leucite, and analcime are also discussed. Experiments were made on the influence of the concentration of the solutions used; in general with concentrated solutions only substitution occurred, whilst with dilute there was also decomposition. The application of the results are discussed at length in connection with geological processes and pseudomorphism, especially as regards the alteration of nepheline; from the constitutional formula above given for this mineral, it is seen that natrolite, hydrargillite or diaspore, and mica, in various combinations, could be derived. The hydronephelite derived from nepheline is considered to be a mixture of natrolite and hydrargillite.

L. J. S.

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## Physiological Chemistry.

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**Heat Value of Proteïds in the Organism.** By CAMILLE MATIGNON (*Bull. Soc. Chim.*, 1894, [3], 11, 568—571).—The physiological heat value of proteïd material is less than the physical heat value, chiefly because in the body combustion is incomplete, and the nitrogen leaves it as urea and uric acid. The heat value of uric acid and its allies is calculated from equations. If the nitrogen leaves the body as urea, the physiological heat value of the proteïd is five-sixths the physical heat value; if as uric acid, the proportion is 3 to 4. Such considerations, however, do not take into account the synthetical processes which no doubt occur in the body in the formation of both substances.  
W. D. H.

**Nitrogenous Metabolism.** By ERWIN VOIT and ALEXANDER KORKUNOFF (*Zeit. Biol.*, 1895, 32, 58—175).—This is an account of a series of experiments on dogs, carried out in the well-known manner of the Munich School, on the question particularly of the smallest amount of nitrogenous food compatible with a condition of equilibrium. As the paper does not discuss the question from the point of view of the nitrogenous metabolism in human beings, it practically adds very little to our knowledge of the much debated question whether the nitrogenous requirement of a man is as great as represented by the earlier experiments of Voit.

The bulk of the present paper is concerned with a discussion of the experiments recorded; the experiments themselves may be stated very shortly.

The dog was fed on a known diet, and its excreta examined. The amount of nitrogen in the food was varied. In some cases the amount was found in which there was no difference in the nitrogenous intake and output. In the majority of instances, however,

this was not exactly the case, but a certain amount of nitrogenous food was found to lead to a loss of a small amount of nitrogen from the body; a small increase led to a gain of some nitrogen to the body; the physiological proteid minimum, that is, the amount just sufficient to maintain equilibrium, is between the two. The experiments are in three categories, the diet in which consisted respectively of (1) proteid alone, (2) proteid *plus* fat, and (3) proteid *plus* carbohydrate. The following table gives some of the main results, in which it will be seen that the physiological proteid minimum is largely diminished in a mixed diet.

*Physiological Proteid Minimum in Grams.*

Dog.	1. Proteid alone.	2. Proteid <i>plus</i> fat.	3. Proteid <i>plus</i> carbohydrate.
1	12.04	7.63	> 4.91
2	> 6.8 < 12.87	> 5.72	5.0
3	> 9.62	> 6.93	5.11
4	> 12.56 < 30.14	5.12	< 4.47

W. D. H.

**The Liver and Metabolism of Carbohydrates.** By FRIEDEL PICK (*Chem. Centr.*, 1894, ii, 55—56; from *Arch. exp. Path. Pharm.*, 33, 305—317).—The liver substance was destroyed by injection of weak acid into the bile duct. This causes the disappearance of glycogen, but no glycosuria. Breathing of carbonic oxide produces glycosuria when glycogen is still present, but in those animals in which it has been made to disappear there is no glycosuria. Thus the sugar in the urine comes from the hepatic glycogen.

The phenomena of phloridzin diabetes have suggested that the sugar in the urine comes not from glycogen, but from proteid. The present method of experiment is a means of determining whether the integrity of the liver is essential for its production, and it was found that it is not. In phloridzin diabetes, the source of the sugar is therefore outside the liver. The formation of glycuronic acid and of urochloralic acid from chloral also occurs after the destruction of the liver substance.

W. D. H.

**Sugar and Cells.** By MAX CREMER (*Zeit. Biol.*, 1895, 32, 49—57).—The bulk of the paper is speculative. It insists on the importance of experiments on yeast and yeast glycogen in order to ascertain what varieties of sugar can form glycogen. The statement that sugars which undergo the alcoholic fermentation with yeast are also true formers of glycogen, and that those which do not ferment are not, is too wide; it does not include the formation of glycogen from mannose and galactose. That those sugars which ferment most easily go into the urine with the greatest difficulty, and those which do not ferment go with the greatest ease, is stated to be true. The rela-

tionship of glycogen to fat formation is also discussed, but no very positive statement made. W. D. H.

**Glycolysis in Blood and Tissues.** By WILHELM SPITZER (*Pflüger's Archiv.*, 1895, **60**, 303—339).—The power that the blood possesses of destroying sugar has been the subject of numerous recent researches. The present research shows that this power is possessed by the blood drawn without admixture, and also by defibrinated, laky, and oxalated blood. This is a property possessed not by the serum, but by the corpuscles. Glycolysis, moreover, is not a vital process, but the blood corpuscles contain substances which possess the power in question. Other tissues are also glycolytic; in fact, glycolysis is a property common to all cells. The disappearance of sugar is due to oxidation; sugar is not destroyed in blood or tissues free from oxygen. The action does not appear to be due to any enzyme, but is the result of the activity of molecular oxygen. A large amount of the paper is devoted to comparing this oxidation with that produced by hydrogen peroxide and other inorganic and organic oxidising agents. W. D. H.

**Thiocyanic acid in the Juices of the Stomach.** By MARCELLUS NENCKI (*Ber.*, 1895, **28**, 1318—1320).—Thiocyanic acid is contained in the juices of the stomach (free from saliva) to the extent of 5 milligrams per litre. It is not contained in muscle or liver; with blood a doubtful result was obtained. C. F. B.

**Paramucin.** By KATHARINA MITJUKOFF (*Archiv. f. Gynäkol.*, 1895, **49**, Heft 2; *Inaug. Diss.*, Berlin).—The colloïd material formed in ovarian cysts may be of two kinds: (1) colloïd which after boiling with acids reduces Fehling's solution, and is generally combined with proteïd matter, as metalbumin or paralbumin; the chief constituent of both these substances was termed pseudomucin by Hammarsten. (2) Colloïd which reduces Fehling's solution without treatment with acid. This is termed paramucin in the present research. It is a jelly-like material, which unites with hydrochloric acid, and was thus separated from the contents of the cysts. By boiling with this acid, it is destroyed, forming a humus-like material. By decomposition with alkalis, it yields an albuminate, an albumose, and a carbohydrate. The carbohydrate does not form an osazone, neither does it ferment with yeast. W. D. H.

**Visual Purple.** By WILLIE KÜHNE (*Zeit. Biol.*, 1895, **32**, 21—28).—Bile is the best solvent of the visual purple. To obtain a solution free from hæmoglobin is difficult in most animals, although it can be accomplished with frogs' eyes. It is, however, now possible to obtain a separation of visual purple from hæmoglobin should both be in solution. The solution in bile salts is saturated with magnesium sulphate; this precipitates the visual purple, hæmoglobin remaining in solution. Saturation with ammonium sulphate precipitates both pigments. After the purple has been fixed in the retina by means of alum, it is comparatively insoluble; it can, however, be dissolved by a

10 per cent. solution of sodium chloride in bile, and is by this method also obtained free from hæmoglobin.

The best method of preserving the purple is to saturate its solution with sodium chloride. This produces a slight cloudiness, but no precipitation of the pigment itself. W. D. H.

**Action of Intravenous Injection of Sodium Chloride Solution on the Composition of Blood and Lymph.** By WELHELM COHNSTEIN (*Pflüger's Archiv.*, 1895, **60**, 291—295).—Further experiments are recorded, which, performed in a somewhat different way, support the author's previously expressed views (compare this vol., ii, 173). W. D. H.

**Abnormal Excretion of Sulphur in a Dog.** By WILLIAM J. S. JEROME (*Pflüger's Archiv.*, 1895, **60**, 233—249).—The manner of excretion of sulphur varies under many circumstances, disease, drugs, hunger, time of day, kind of food, kind of animal, &c. The present extended series of experiments were all made on one dog, and show that during a normal period 66·5 per cent. of the total sulphur was excreted as sulphuric acid; this rose to 68·4 per cent. on the administration of carbaminthioglycollic acid, and fell to 50·4 on the administration of ethylic sulphide. The drugs produced not only an effect while being given, but the effect lasted some time after; calomel and jalap produced a rise to 70 per cent. Simultaneous observations on the nitrogen excreted showed that the differences are absolute, and not merely relative to the amount of proteid metabolism. W. D. H.

**Physiological Action of Hydrohydrastininum Hydrochloride.** By WILLIAM KRAMM (*Chem. Centr.*, 1894, ii, 59—60; *Dissert.*, Berlin).—Hydrohydrastinine causes reflexly clonic, sometimes tetanic, convulsions; it is not toxic to the heart, but increases the rate and pressure of the blood flow. This is well marked after the fall of pressure accompanying vagus stimulation. Before convulsions set in, the drug causes dyspnoea. W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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**The Time of Trehalose Formation in Plants.** By EMIL E. BOURQUELOT (*Chem. Centr.*, 1894, ii, 482; from *Bull. de la Soc. mycol. de France*, 9, 11).—In species the development of which proceeds uninterruptedly from the germination of the spore, trehalose is formed in appreciable quantity only at the time of spore formation, which, for that matter, occurs very early in the case of these species. In such species as at certain times form a sclerotium, in order to await more favourable conditions for fructification, the state of matters is more complicated: some behave like those already mentioned; in

others the sclerotium develops trehalose even during the period of stagnation. The trehalose is formed from a reserve substance contained in the tissues, probably from a carbohydrate analogous to dextrin.

C. F. B.

### Variations in the Sugars during the Germination of Barley.

By PAUL PETIT (*Compt. rend.*, 1895, **120**, 687—689).—Experiments with two lots of barley show that during steeping the variations in the proportions of reducing sugar are trifling, whilst the quantity of saccharose continually increases. The results were as follows in milligrams of sugar per 1000 barley grains.

	Original.	1st day.	2nd day.	3rd day.	4th day.	5th day.
Reducing sugar (as glucose) .....	24	29	30	31	32	39
Saccharose .....	214.7	230	260.3	307	384.8	406.6

The following results were obtained during germination.

	On malting floor.			In Saladin's apparatus.		
	Glucose.	Saccharose.	Diastatic power.	Glucose.	Saccharose.	Diastatic power.
1st day .....	48	413	0	57	403	0
2nd „ .....	86	420	0	84	435	0
3rd „ .....	187	426	0	172	457	0
4th „ .....	269	433	564	234	462	525
5th „ .....	319	437	225	287	464	195
6th „ .....	363	453	143	341	469	125
7th „ .....	394	476	83	379	489	66
8th „ .....	417	542	34	409	553	31
9th „ .....	402	642	31	397	651	28
After drying.	330	782	150	324	826	100

There would seem to be a relation between the quantity of reducing sugar and the activity of respiration. There is also a relation between the quantities of reducing sugar and of saccharose in the barley during its germination. Pneumatic malting gives more regular respiration, and yields a malt richer in diastase even after drying.

C. H. B.

**The Sugar of the Agave Americana.** By WINTHROP E. STONE and DUMONT LOTZ (*Amer. Chem. J.*, 1895, **17**, 368—371).—In 1892 Michaud and Tristan stated (*Abstr.*, 1893, i, 94) that they had obtained a new crystalline and inactive sugar from the *Agave Americana*, to which they gave the name agavose. The authors have carefully reinvestigated this matter, but find that the only crystallisable sugar in the *Agave* juice is saccharose. The non-activity of the sugar obtained by Michaud and Tristan must have been due to the impurity of their specimen; the juice contains some invert sugar. The carefully purified sugar obtained by the authors had a specific rotation  $[\alpha]_D =$

+66.3°, and showed all the characteristics and reactions of saccharose. On inversion, it yielded invert sugar having the specific rotation  $[\alpha]_D = -20.6^\circ$ . L. T. T.

**The Organic Bases of some Agricultural Seeds, Oil-cakes, Tubers, and of some Seedlings.** By ERNST SCHULZE, S. FRANKFURT, and ERNST WINTERSTEIN (*Landw. Versuchs-Stzt.*, 1895, **46**, 23—77).—Choline occurs in the seeds of *Vicia sativa*, *Pisum sativum*, and *Cannabis sativa*, in seedlings of *Triticum vulg.* and *Arachis hypogæa*, in cocoa-nut palm and sesame cake, in potatoes, in etiolated seedlings of *Vicia sat.*, *Lupinus luteus* and *alb.*, *Soja hispida*, and *Cucurbita pepo*, and in malt sprouts. Choline is accompanied by betaine in the sprouts of wheat and malt. Trigonelline was found in the seeds of peas, hemp, and oats (compare E. Jahns, *Abstr.*, 1886, 85; 1891, 1520; R. Böhm, *Arch. exper. Path. u. Pharmacol.*, **19**, 60 and 87; Griess and Harrow, *Trans.*, 1885, 298; Kunz, *Arch. Pharm.*, **223**, 701; Brieger, *Zeit. physiol. Chem.*, **11**, 184, and v. Lippmann, *Abstr.*, 1888, 314).

As regards the possibility of the choline having been produced from lecithin during the treatment of the extracts, this would only be possible in the case of alcoholic extracts, since lecithin is insoluble in water. And in the case of alcoholic extracts, the evidence is against such an assumption. No other compound is as yet known to occur in plants which yields choline as a decomposition product.

Betaine had previously been found in cotton seed (Ritthausen and Weger, *J. pr. Chem.*, [2], **20**, 32) in the seeds of *Artemisia Cina* (Jahns, *Abstr.*, 1893, ii, 485) and of *Chenopodium album* (Halpern, *Ber. physiol. Lab. Versuchsaut. d. Landw. Inst. Univ.*, Halle, Heft. 11, 72), and in the leaves of *Solanum tuberosum* (Schütte, *Arch. Pharm.*, **229**, 492). In the plants examined by the authors, betaine probably occurs ready formed, except possibly in the case of vetch seeds (compare Scheibler, *Ber.*, **3**, 159, and Liebreich, *ibid.*, 161).

Trigonelline is only known to occur in *Trigonella fœnum græcum* (Jahns, *loc. cit.*), besides the plants given above.

Choline alone of the bases isolated is known to act poisonously; stachydrin has not yet been examined. Inasmuch as the greatest amount of choline found was about 0.05 per cent., it cannot be considered dangerous; at the same time, it has been known to be injurious (Böhm, *loc. cit.*).

The amount of choline is higher in etiolated sprouts than in seeds; at the same time, there is a corresponding diminution in the amount of lecithin.

Only bases soluble in water or alcohol were investigated, and of these only a portion. The methods of separation are fully described. N. H. J. M.

**Essence of Roots of Polygala from Java.** By PIETER VAN ROMBURGH (*Rec. Trav. Chim.*, 1894, **13**, 421—424).—The roots of *Polygala variabilis*, *D. C. oleifera*, Haeckel, and *Javana* yield, on distillation with steam, small quantities of a heavy oil, sp. gr. = 1.174 at 27°, b. p. 222°, consisting almost entirely of methylic salicylate. The

amount obtained, in each case, from 2 kilos. of roots was only about 1.5 c.c. JN. W.

**Volatile Principles of Coca Leaves from Java.** By PIETER VAN ROMBURGH (*Rec. Trav. Chim.*, 1894, **13**, 425—428).—On exposing some fresh coca leaves (*Erythroxylon coca*, Lamarck) to air charged with chloroform vapour, they behaved in the same way as tea leaves, darkening in colour, and acquiring a fragrant odour, and as the odour resembled that of the roots of *Polygala* (preceding abstract), the darkened leaves were distilled with steam, with the result that, as in the former case, it proved to be due to methylic salicylate. This, however, had not been formed or liberated by the action of the air or chloroform, as it can be isolated from the untreated leaves, and occurs, moreover, like the vegetable alkaloids and other products of development, in greatest quantity (0.12 per cent.) in the youngest leaves. The product from 140 kilos. of leaves appeared to contain, in addition, salicylaldehyde and acetone. Other species of erythroxylon gave the same results. JN. W.

**The Resin of German Pines.** By HEINRICH MAYR (*Bied. Centr.*, 1895, **24**, 254—255; from *Bot. Centr.*, 1894, **59**, 52).—Of the various parts of the trees, the root-wood is richest in resin, next the stem to a height of 2 m., and the branches; the bark is the poorest in resin. The south half of the trunk is always richer than the north half, and the upper sides of roots and branches richer than the under sides. The amount of resin increases with the age of the trees, and is greater in warm positions and in trees growing in light soil. Only growing cell membrane is permeable to resin; fully developed cell walls, whether woody or not, do not allow the passage of resin as long as they are saturated with water. N. H. J. M.

**Composition of Oat Plants.** By ALBERT ATTERBERG (*Bied. Centr.*, 1895, **24**, 259—262; from *Årsberättelse f. Kalmar kem. stat. f. året.*, 1888—89; compare *Abstr.*, 1888, 317).—By growing oats in nutritive solutions rich in phosphates, the percentage of nitrogen was reduced to 0.25 per cent. in the straw, and was 1.50 to 1.40 in the grains. When increasing amounts of nitrogen were given to the plants, the percentage of nitrogen remained fairly constant; but with still larger amounts of nitrogenous manure, an increase in the percentage of nitrogen of the produce was observed, especially when less phosphoric acid was applied.

European barley becomes gradually poorer in nitrogen, whilst in America the crops are still very rich in nitrogen; this is probably due to greater use of phosphates in Europe than in America. As a rule, the relation  $N_2 : P_2O_5$ , both in oat grain and in green oats, varies proportionally with the relation in the manure. When this relation is greater than 1.7 : 1.0, phosphatic manure is more necessary than nitrogenous. When the relation is less than 1.6 : 1.0 nitrogenous manure is wanted.

The percentage of potash varies only slightly in oat grain, but in the straw may vary from 0.3 to 5.0 per cent. In straw, potash may



be replaced to a considerable extent by soda. Straw containing as little as 0·37 to 0·38 per cent. of potash is unhealthy; with insufficient soda present, the disease appears when the straw contains as much as 1·0 per cent. of potash.

In oats grown under natural conditions, the relation between nitrogen, phosphoric acid, and potash varies as follows:—100 : 21—67 : 21—173; when grown on peaty soil the relation is 100 : 33 : 62.

N. H. J. M.

**Composition of different kinds of Berries.** By ALBERT EINECKE (*Landw. Versuchs.-Stat.*, 1895, **46**, 21—22).—Analyses of six varieties of gooseberries and five varieties of currants were made, including amount of sap, sugar, free acid, extract, nitrogen, ash, and phosphoric acid in ash. To ascertain whether the differences in composition are due to the special characters of the varieties or to conditions of cultivation, weather, &c., the investigation will have to be continued for some years.

N. H. J. M.

**Composition of Soils from South India.** By CECIL MASSEY (*Chem. News*, 1895, **71**, 261—262).—Analysis of four arable soils, bearing coffee, from Coorg, South India, gave the following numbers per cent.

	I.	II.	III.	IV.
Moisture.....	6·68	6·22	7·02	7·42
Organic matter and combined water.....	3·70	4·30	3·97	4·84
Fe <sub>2</sub> O <sub>3</sub> .....	4·20	3·82	5·00	3·32
Al <sub>2</sub> O <sub>3</sub> .....	5·40	6·22	6·19	6·83
CaO.....	0·86	0·99	0·82	1·00
MgO.....	0·21	0·30	0·26	0·35
K <sub>2</sub> O.....	0·62	0·73	0·58	0·68
Na <sub>2</sub> O.....	0·38	0·34	0·30	0·41
P <sub>2</sub> O <sub>5</sub> .....	0·40	0·57	0·71	0·81
SO <sub>3</sub> .....	0·12	0·21	0·19	0·20
CO <sub>2</sub> .....	0·21	0·30	0·19	0·24
Cl.....	0·02	0·03	0·09	0·08
SiO <sub>2</sub> and insoluble.....	77·20	75·97	74·68	73·83
N per cent. in organic matter.....	0·69	0·83	0·79	0·86
Specific gravity.....	2·50	2·56	2·46	2·39

Bacteriological examination showed the following number of microbes per gram of each soil: I, 196,000; II, 253,000; III, 210,000; IV, 264,000.

D. A. L.

**Effect of Sulphurous acid on Soil and on its Produce.** By A. DAMSEAUX (*Bied. Centr.*, 1895, **24**, 279; from *Influence des dégagements d'anhyd. sulfureux sur les terres et sur la production*, Brussels, 1894).—The effect of sulphurous acid is to increase the percentage of ash constituents, especially in meadow and pasture grasses. Silica, iron, and aluminium increase, whilst phosphoric acid and potash decrease. As the amounts of proteids and fat diminish, there is also

a diminution in the digestibility of the proteïds. The plants produced illness in the animals which consumed them.

N. H. J. M.

**Amount of Nitrogen in the Humus in Soils of Arid and Humid Regions.** By EUGEN W. HILGARD and MEJER E. JAFFA (*Bied. Centr.*, 1895, **24**, 218—219; from *Agric. Science*, **8**, 165—171).—Soils from the humid regions of the Mississippi and from Louisiana yielded humus (by Grandean's method) containing from 4 to 5 per cent. of nitrogen. In upland soils, the amount of humus was rarely as much as 0·5, and often less than 0·2 per cent. Nitrogenous manures on such soils were, however, frequently without effect, or even injurious, indicating that the humus of rich soils must be unusually rich in nitrogen. The following average percentage results are given. The numbers in brackets indicate the number of samples.

	Per cent. of humus in soil.	Nitrogen.	
		In humus.	In soil.
Upland (arid) soil. California (18) .....	0·75	15·87	0·101
Lowland (arid) soil. California (8) .....	0·99	10·03	0·102
Humid soil from arid and humid regions of California (5) .....	1·86	5·03	0·088
Humid soils—other States (5) .....	5·04	5·24	0·132

The differences between the amounts of nitrogen in the soils of arid districts and those of humid soils are very striking. In some cases the humus was richer in nitrogen than proteïds generally are. A strongly alkaline soil containing much sodium carbonate, and considerable quantities of sodium nitrate and phosphate, and potassium sulphate, yielded an inky black extract, from which humus containing 17 per cent. of nitrogen was obtained.

The humus of porous soils is, as a rule, poorer in nitrogen than that of dense soils; a high percentage of alkaline earthy carbonates is favourable to accumulation of nitrogen.

N. H. J. M.

**Utilisation of the Nitrogen of Farmyard Manure and of Green Manure.** By JULIUS KÜHN (*Bied. Centr.*, 1895, **24**, 222—223; from *Deut. Landw. Presse*, 1894, No. 15, 22, 33, 34, 48—51).—The author maintains, in opposition to Wagner, that the nitrogen of farmyard manure is more used up than that of green manure. According to the kind of food, 56 to 80 per cent. of the nitrogen of dung should be available to plants in the first year. Wagner's experiments were not suited to decide the question, as unequal amounts of nitrogen were applied to the different plots, and the farmyard manuring was excessive.

N. H. J. M.

## Analytical Chemistry.

**Apparatus for Rapid Calibration of Measuring Vessels.** By J. C. BOOT (*Rec. Trav. Chim.*, 1894, **13**, 417—425).—A column of 10 bulbs, each containing accurately 10 c.c. from mark to mark on the tubes connecting them, is connected at the base, through a three-way tap, with the base of a 10 c.c. burette, graduated in 1/50 c.c. The apparatus is filled through a second tap at the base of the bulb burette, and either branch can be discharged through the third-way of the three-way tap. The vessel to be calibrated is filled from the bulb burette, and the excess or defect from the reputed volume measured by means of the fine burette. In calibrating a 50 c.c. flask, for example, the bulb burette is filled to the 50 c.c. mark, the fine burette to the 10 c.c. mark, and the flask is filled from the former. If its capacity is less than that reputed, the liquid in the bulb burette will remain above the zero mark, and the difference is measured by refilling the lowermost bulb through the three-way tap from the fine burette, and noting the amount remaining in the latter. If, on the other hand, the capacity is greater than the reputed capacity, the flask will not be quite filled by the contents of the bulb burette, and the excess is measured by direct addition from the fine burette.

Sulphuric acid of sp. gr. 1.2 is recommended as the calibrating liquid, as it does not adhere to the glass, and is neither hygroscopic nor liable to evaporation.  
JN. W.

**Standardising Acid Solutions.** By EDGAR P. PERMAN and W. JOHN (*Chem. News*, 1895, **71**, 296).—It is suggested that borax should be used for standardising sulphuric or hydrochloric acid, methyl-orange being used as indicator [compare Salzer (*Abstr.*, 1894, ii, 27) and Rimbach (*Abstr.*, 1893, ii, 233)].  
D. A. L.

**Carius-Volhard Estimation of Halogens.** By JAMES WALKER and JAMES HENDERSON (*Chem. News*, 1895, **71**, 295—296).—F. W. Küster, finding that silver nitrate acts on the glass if used in excess in the Carius method, takes exception to the method described by the authors (this vol., ii, 326); but they point out that such action does not take place to a serious extent below 280°, and as the reaction can be completed at 250—260° (by using 2 c.c. of nitric acid, sp. gr. 1.5, instead of the smaller quantity used by Küster), volumetric results, agreeing well with the gravimetric numbers, are obtained, as exemplified by the numbers for the halogens in paradichloro- and paradibromo-benzene given in the paper.  
D. A. L.

**Estimation of Sulphurous and Sulphuric acids in the Products of Combustion of Coal-gas.** By UNO COLLAN (*Zeit. anal. Chem.*, 1895, **34**, 148—158).—From the results of experiments by Young and others, it has hitherto been considered that the sulphur in coal-gas is mainly oxidised to sulphuric acid during the combustion.

The author shows experimentally that Young's method of absorbing the products of combustion by an alkali is misleading, inasmuch as sulphurous acid mixed with air is oxidised to sulphuric acid under these conditions. But when the products of combustion (from a non-luminous Bunsen flame) are allowed to act directly on chromic acid, a quantity of the chromic acid is reduced, which corresponds with the presence of 89—99 per cent. of the sulphur in the form of sulphurous acid. Since no other cause for the reduction of the chromic acid could be detected, the author concludes that the chief product of the combustion of the sulphur is not sulphuric, but sulphurous, acid.

M. J. S.

**Detection and Estimation of Selenium in Meteoric Iron.** By HENRY N. WARREN (*Chem. News*, 1895, **71**, 249—250).—Ten grams of filings of the iron is mixed with sufficient flowers of sulphur and heated to redness in a combustion tube in a current of oxygen; the sulphurous and selenious anhydrides produced pass into a series of bulb-tubes containing water in which the selenium collects. This is heated while in the liquid to 27°, and the selenium is then dried in an air-bath in a platinum dish. In six specimens of meteoric iron examined the following quantities of selenium have been found:—0.23, 0.05, 0.04, 0.06, 0.08, and 0.05 per cent.

D. A. L.

**Apparatus for Measuring out Small Drops of Mercury for Kjeldahl's Process.** By PAUL LIECHTI (*Zeit. anal. Chem.*, 1895, **34**, 169—170).—This is, externally, exactly like a stopcock separator, but the plug of the stopcock, instead of being pierced, has at one side a conical cavity of such size as to contain the required quantity of mercury. This fills when placed upwards, and delivers its charge when the plug is turned through 180°.

M. J. S.

**Estimation of Nitric Nitrogen in Presence of Organic Nitrogen.** By THEODOR PFEIFFER and H. THURMANN (*Landw. Versuchs-Stat.*, 1895, **46**, 1—20).—Of the methods generally employed, reduction with zinc dust in alkaline solution gave unsatisfactory results with urine, whilst Schloesing's method is liable to give rise to loss of nitrogen in presence of organic matter owing to the action of nitric oxide on ammonia or on urea.

The following method was found to yield good results. The liquid contained in a Linter pressure flask is treated with about 10 grams of caustic soda, and heated at 120—130° for about eight hours. When cold, the contents of the flask are poured into a distilling flask, the solid matter washed on to a filter and dried. The liquid is treated with a further quantity of caustic soda and boiled until no more ammonia is evolved. The dried precipitate is then put into the flask, washing the paper with acetic acid and water to remove the last traces, and the whole reduced with zinc-iron in the usual manner. The distillation must be carefully done owing to frothing. It seems impossible to obtain caustic soda free from nitrates, but if the same quantity is always employed, a correction can be made. For many substances, boiling with alkali is sufficient.

Ammonia may be generally estimated in farmyard manure, &c., by

distilling with magnesia. Commercial urea when distilled with magnesia yields ammonia, but this is shown to be due to ammonium carbonate present as an impurity. Urea which has been precipitated with nitric acid gives no ammonia.

The following method is given for preparing faeces for analysis. The faecal matter is emptied into sifted peat meal (15 to 20 per cent.), quickly mixed and dried after addition of acid. An odourless, friable mass is obtained, from which good samples are readily taken. The exact amount of peat and its composition must, of course, be known.

N. H. J. M.

**Practical Working of Pelouze's Process.** By VINCENT EDWARDS (*Chem. News*, 1895, **71**, 307).—Ten grams of the nitrated manure is dissolved, filtered, and made up to 200 c.c.; 20 c.c. of this solution and 50 c.c. of a solution containing 100 grams of ferrous sulphate and 100 c.c. of strong sulphuric acid per litre, are run into a 600 c.c. flask, fitted with a rubber stopper and a Bunsen valve, and boiled until the liquid becomes viscid. The flask is enveloped in a cloth as a precaution in case of fracture, and, when cool, 100 c.c. of water is added, and even if all the material in the flask is not very soluble, the solution is titrated with a solution containing 14.742 grams of potassium dichromate per litre, until a bright yellow colour is obtained with a drop of ferricyanide.

D. A. L.

**Preparation of Thioacetic acid, and its Application in Chemico-legal Investigations.** By ROBERT SCHIFF (*Ber.*, 1895, **28**, 1204—1206; compare this vol., ii, 84).—In preparing thioacetic acid by acting on glacial acetic acid with phosphorus pentasulphide, addition of crushed glass is found to prevent the frothing which usually takes place in the distilling flask. Rectified, thioacetic acid is free from arsenic, and this metal may be determined quantitatively by its means; the necessity of providing a continuous stream of hydrogen sulphide free from arsenic is therefore obviated, as the quantitative decomposition of arsenious and arsenic acids is effected by boiling the solution in hydrochloric acid for a few minutes with thioacetic acid.

M. O. F.

**Analysis of Organic Compounds containing Boron and Fluorine.** By V. GASSELIN (*Ann. Chim. Phys.*, 1894, [7], **3**, 69—78).—See this vol., i, 453.

**The Inclusion of Barium Chloride by Barium Sulphate.** By THEODORE W. RICHARDS and HARRY G. PARKER (*Zeit. anorg. Chem.*, 1895, **8**, 413—423).—The authors have determined the amounts of barium chloride included in the precipitate when sulphuric acid is estimated as barium sulphate. The sulphuric acid solution contained 3.214 per cent. of sulphuric acid as determined by titration with pure sodium carbonate. It was estimated by precipitation with barium chloride, taking all known precautions to prevent the inclusion of barium chloride in the precipitate. The precipitate was separated, and the filtrate evaporated to a small bulk in order to obtain the dissolved barium sulphate. The whole precipitate was then fused with pure sodium carbonate, and the chlorine in the aqueous solution of

the melt determined as silver chloride. The chlorine is then calculated into barium chloride, and the weight of the latter subtracted from that of the barium sulphate. The results of two tests, without the correction, for included barium chloride gave 3.218 per cent.  $\text{H}_2\text{SO}_4$ ; when corrected for barium chloride they gave 3.214 per cent.  $\text{H}_2\text{SO}_4$ . The mean result of 17 experiments, in which the precipitation of the barium sulphate was performed with the ordinary precautions, was 3.215 per cent.  $\text{H}_2\text{SO}_4$  without correction, and 3.200 per cent. when corrected for included barium chloride, which shows that the solubility of the barium sulphate nearly eliminates the error due to the inclusion of barium chloride. An excess of barium chloride does not increase the error due to inclusion. This error is, however, greatly increased by adding the sulphuric acid to the barium chloride instead of *vice versa*, and, also, it is enormously increased by the presence of a large quantity of hydrochloric acid. The error is diminished by dilution of the solutions, and also by stirring, whilst the barium chloride is being added.

E. C. R.

**Volumetric Estimation of Zinc.** By LÉONCE BARTHE (*Bull. Soc. Chim.*, 1895, [3], 13, 82—85).—Fresh tincture of hollyhock is not affected by the common inorganic salts of zinc, but is turned green by alkali; excess of acid in solutions of zinc can, therefore, be directly titrated. On the other hand, zinc solutions become neutral to phenolphthaleïn only when enough alkali has been added to form a basic salt,  $\text{ZnSO}_4 \cdot 4\text{ZnO}$ . By combining these two processes, zinc can be titrated in solutions of its nitrate and sulphate.

The salt (1/1000 equivalent) is dissolved in water or dilute acid (to 100 c.c.), and an aliquot portion (10 c.c.) diluted (to 100 c.c.), and titrated for free acid; a second portion is titrated with alkali in presence of phenolphthaleïn. The percentage of zinc is equal to the difference between the two titres in c.c. of decinormal alkali multiplied by the factor  $0.00325 \times 1.25$ .

JN. W.

**Separation of Copper and Cadmium.** By ALLERTON S. CUSHMAN (*Amer. Chem. J.*, 1895, 17, 379—383).—Cadmium sulphide dissolves readily in a saturated solution of the alkali chlorides in the presence of dilute hydrochloric acid. The reaction probably takes place according to the equation  $\text{CdS} + 2\text{RCl} + 2\text{HCl} = \text{CdCl}_2 + 2\text{RCl} + \text{H}_2\text{S}$ . Copper sulphide is not attacked at all under these conditions, and the reaction thus serves as a very delicate means of detecting minute traces of cadmium in the presence of copper. The test is best carried out as follows. About 2 c.c. of the solution containing the two metals is made slightly acid with hydrochloric acid, and about 20 c.c. of a saturated solution of sodium chloride added. Hydrogen sulphide is passed until the copper is entirely precipitated, and the precipitate then filtered off through a dry filter, and the filtrate run into a dry test tube. On dilution of the filtrate, the cadmium sulphide is precipitated. It is best to allow a few drops of water to run down the side of the test tube, when a yellow line of cadmium sulphide is formed at the junction of the two liquids. If the amount of cadmium present is very small, it is best to use very dilute ammonia instead of

water, as the yellow line is developed more quickly. If the separation of the other metals (lead, bismuth, &c.) is incomplete, however, they somewhat mask the reaction, especially if ammonia is employed. 0.1 milligram of cadmium can be at once detected by this method, whilst with 0.01 milligram a yellow ring develops in half an hour. The reaction is much more delicate than either the cyanide or sulphuric acid methods for separating copper and cadmium.

L. T. T.

**Estimation of Antimony as Tetroxide.** By OTTO BRUNCK (*Zeit. anal. Chem.*, 1895, **34**, 171—174).—This method has latterly fallen into discredit, in consequence of the statement by Bunsen that the tetroxide is reduced to trioxide and volatilised at a temperature only a little higher than that at which it is formed. This, however, is shown to be incorrect, provided that reducing gases from the flame are completely excluded. In an uncovered crucible neither reduction nor loss of weight takes place; but with the lid on reduction occurs even when the flame surrounds only the lower half of the crucible. By supporting the crucible in a closely-fitting ring of asbestos board, access of reducing gases is prevented, and a cover can be employed. From weighed quantities of antimony, whether in the form of metal, or as sulphide, the amount of oxide obtained agreed exactly with the formula  $\text{Sb}_2\text{O}_4$ , and with access of air a constant weight was rapidly attained. The method is, therefore, thoroughly trustworthy.

M. J. S.

**Estimation of Thiophen in Benzene.** By GEORGES DENIGÉS (*Compt. rend.*, 1895, **120**, 781—783).—In order to estimate thiophen in the form of the compound,  $2\text{HgSO}_4, 2\text{HgO}, \text{C}_4\text{SH}_4$  (this vol., i, 411), 20 c.c. of the reagent (containing mercuric oxide, 50 parts; sulphuric acid, 200 parts; water, 1000 parts) is mixed with 2 c.c. of the benzene in a flask of 60 c.c. capacity, the stopper is tightly tied down, and the flask heated on a water bath for about 15 minutes, with occasional vigorous agitation. The precipitate is washed with boiling water, and dried at  $110\text{--}115^\circ$ ; its weight multiplied by 0.0758 gives the weight of thiophen. The results are satisfactory, although always very slightly too low.

If the reagent (1 part) is mixed with methylic alcohol (3 parts) free from acetone, the reaction will take place at the ordinary temperature, since the alcohol dissolves the benzene; 10 c.c. of the mixture is agitated with 1 c.c. of the benzene, and 1 part of thiophen in 100,000 can be detected.

In aqueous solutions the composition of the precipitate remains constant, whatever the proportions of thiophen and mercuric salt, but in presence of methylic alcohol this is no longer the case, and a definite compound is obtained only when the mercury is in excess with respect to the thiophen, and the precipitate then has the composition,  $\text{HgSO}_4, 2\text{HgO}, \text{C}_4\text{SH}_4$ .

To make an estimation at the ordinary temperature, 2 c.c. of benzene is dissolved in 30 c.c. of methylic alcohol, and 10 c.c. of the mercury solution is added rapidly, and the mixture agitated; after about 20 minutes the precipitate is washed with boiling water and

dried. Its weight, multiplied by 0.1034, gives the weight of thiophen. The results quoted are very satisfactory. C. H. B.

**Preservative Value of Formaldehyde and its Detection in Milk.** By ROBERT T. THOMSON (*Chem. News*, 1895, 71, 247—248).—In comparative experiments the author has found that as a preservative for milk,  $8\frac{3}{4}$  grains per gallon of formaldehyde is as effective as 35 grains of salicylic acid, or 35 grains of boric acid, half as free acid, half as borax, and that it surpassed 35 grains of free boric acid, or  $17\frac{1}{2}$  grains of benzoic acid.

To detect formaldehyde in milk, 20 c.c. is carefully distilled from 100 c.c. of milk, and placed in a stoppered tube with 5 drops of a solution, prepared by dissolving 1 gram of silver nitrate in 30 c.c. of water, adding just sufficient dilute ammonia to redissolve the precipitate first formed, and making up to 50 c.c. with water. The tube is set aside in the dark, and the presence of formaldehyde is indicated by the formation of a black (not brown) deposit, which may take 12 to 18 hours to form, if only a small quantity of formaldehyde is present; as little as 2 grains per gallon may be detected in this manner.

D. A. L.

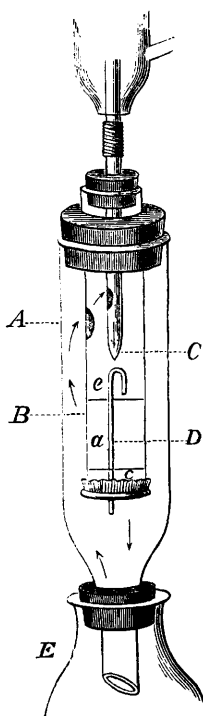
**Precipitation of Uric acid and Xanthine Derivatives.** By MARTIN KRÜGER (*Chem. Centr.*, 1894, ii, 483; from *Du Bois-Reymond's Archiv.*, 1894, 374—378).—Uric acid, hypoxanthine and adenine (compare Abstr., 1894, ii, 74) can be completely precipitated as cuprous compounds—of the formula  $C_5H_3Cu_2N_5$  in the case of adenine—by adding copper sulphate and sodium hydrogen sulphite; the precipitates dissolve respectively in 560,000, 250,000, and 200,000 parts of water. If an attempt is made to estimate uric acid in urine by means of this reaction, 20.6 per cent. more nitrogen is found than by the Ludwig-Salkowski method. This excess of nitrogen is due to the precipitation of xanthine and sarcine bases with the uric acid, and the amount of the excess is a measure of the quantity of these bases present. As a mean of 11 experiments with normal urine, the ratio of nitrogen present as bases to that present as uric acid, as determined by the Ludwig-Salkowski method, was found to be 3.82 : 1.

In the estimation of the total nitrogen of both bases and uric acid, 100 c.c. of urine is heated to boiling, 10 c.c. of commercial saturated sodium hydrogen sulphite solution, and 10 c.c. of a 13 per cent. copper sulphate solution are added, the whole is then heated to boiling again, treated with 5 c.c. of 10 per cent. barium chloride solution, and set aside. After two hours, the liquid is filtered through a folded filter, the precipitate washed five times with hot water, and the nitrogen in it determined by the Kjeldahl method.

C. F. B.

**A New Method of estimating Fat in Milk.** By A. N. NAHM (*Chem. Centr.*, 1894, ii, 669—670; from *Milch. Zeit.*, 23, 555—558).—One hundred c.c. of milk is heated to boiling for 25 minutes in a special apparatus, after adding 25 c.c. of a mixture containing 4.5 per cent. potassium hydroxide, 56 per cent. of amylic alcohol, 15.5 per cent. of ethylic alcohol, and 30 per cent. of ammonia. The mixture should be well shaken every five minutes.





A pinch cock being opened, the liquid is now forced by means of an india-rubber valve into a calibrated tube 20 cm. in length, each division of which represents 0.05 per cent. of fat. After standing some time in a water bath, the volume of the fatty layer is read off.

L. DE K.

**Modification of Tollens' Fat-extraction Apparatus.** By UGO MILONE (*Chem. Centr.*, 1894, ii, 642; from *Boll. Soc. Nat. Napoli*, [2], 8, 1—3).—The tube *A* is 25 by 5 cm., *B* is 17 by 3 cm.; the flask, *E*, which contains the boiling ether, has a capacity of 60 c.c. *B* is closed at the lower end by a piece of cloth tied over it; on this is placed a little cotton-wool, freed from fat, then the substance to be extracted, and, above all, a little more cotton-wool. The ether extract drops through the cloth, but in case it should accumulate in *B*, the siphon *D* is added, passing through the cloth; this draws off the ether extract when it has reached the level *e*.

C. F. B.

**Butter.** By CARL T. MÖRNER (*Zeit. anal. Chem.*, 1895, 34, 175).—The author has determined the "baryta number" of numerous specimens of fresh butter from southern and mid Sweden, according to the process of König and Hart (*Abstr.*, 1891, 1301), and finds it to vary from 180 to 228, the average being 200.7, which is a little lower than that (221) found by König and Hart.

M. J. S.

**Iodine Absorption.** By HERMANN BREMER (*Chem. Centr.*, 1894, ii, 496; from *Forschungsber. Lebensm.*, 1, 318—325).—The author thinks the Hübl method a very exact one. When dealing with drying oils, the iodine solution should be allowed to act for 18 hours, and the test performed according to Dieterich's directions. With other oils, two hours are sufficient at a temperature of 15—18°. An excess of 10 per cent. of iodine is sufficient for ordinary oils, 30 per cent. for drying oils. Too large an excess of iodine, or a temperature below 15° or over 30°, affects the accuracy of the results. Contrary to Gantter's statement, stearic acid does not absorb iodine.

L. DE K.

**Pumpkin Oil.** By ARTHUR SCHATTENFROH (*Chem. Centr.*, 1894, ii, 518; from *Zeit. Nahrungsm. Hyg. Waar.*, 8, 202—205).—The oil is pressed from pumpkin seeds, after they have been heated several times. It is insoluble in water and alcohol, soluble in ether, chloroform, benzene, carbon bisulphide, light petroleum, and acetone; its sp. gr. = 0.9226 (0.9234) at 30°; it solidifies at -16°, and the fatty acids obtained from it melt at 25—27°, and solidify at 23—24°; it is optically inactive. It contains 1.52 per cent. of unhydrolysable matter,

8 of glycerol, 80.9 of volatile, and 15.3 of solid insoluble acids; it contains no nitrogen, sulphur, chlorine, or lecithin; it has an acid number of 1.27, a saponification number of 188.7, and an ether number of 187.3. It contains phytostearin; its Reichert-Meissl number is 9.24, its Hehner's number 96.2, its acetyl number 27.2, and its Hübl's iodine number 113.4.

C. F. B.

**New Test for Morphine.** By LIAMAL (*Chem. Centr.*, 1894, ii, 602; from *Semaine Médic.*, 14, 267).—Solutions of morphine give, on addition of uranium acetate, a reddish-brown colour, which disappears on adding acids, whilst, on adding caustic alkalis, a deep red precipitate is formed, which turns yellow on adding an excess of the reagent. The test is best made by putting 2—10 drops of the morphine solution into a porcelain dish and adding the same quantity of uranium solution (0.015 gram of uranium acetate and 0.01 gram of sodium acetate in 5 c.c. of water). After evaporating on the water bath, concentric, bright, or hyacinth-red spots are left. The reaction is still visible with 0.05 milligram of the alkaloid. Oxymorphine gives the same reaction, but toxines and most of the other alkaloids do not. Salicylic acid gives brick-red spots, tannin, gallic acid, and pyrogallol brown ones. Phenol gives a brown colour, slowly disappearing on warming. The coloration with uranium acetate is very permanent, and may serve as evidence in court.

L. DE K.

**Fallacies of Post-mortem Tests for Morphine.** By DAVID L. DAVOLL, jun. (*J. Amer. Chem. Soc.*, 1894, 16, 799—808).—The author's experiments were made on the body of a dog which, after being shot, was buried for 45 days in a tight pine box, with cover screwed on, under five feet of gravelly soil. The various organs were then tested as if poisoning by morphine had been suspected. Portions of the various extracts were also examined after a trace of morphine had been purposely added.

The experiments proved, that when dealing with cadaveric bodies the only trustworthy tests are:—Fröhde's reagent (sulpho-molybdic acid), Le Fort's test (iodic acid), and ferric chloride solution.

L. DE K.

**Estimation of Gelatin and Albumin in Presence of Peptone.** By ERNST O. BECKMANN (*Chem. Centr.*, 1894, ii, 898; from *Forschungsber. Lebensm.*, 1, 423—425).—Formaldehyde precipitates gelatin from concentrated solutions as formalin-gelatin. Dilute solutions evaporated with the reagent also leave the insoluble compound generally mixed with trioxymethylene, which may be extracted with boiling water. Much free acid interferes with the complete precipitation. Peptones (gluten-peptone, meat-peptone) remain soluble; egg-albumin and serum-albumin become insoluble. The author has founded on these tests a quantitative method for separating gelatin from peptones and albumins. The albumin is first precipitated in an aliquot part of the solution by precipitating with acids, and in another part both gelatin and albumin are precipitated by means of formaldehyde. The difference gives the gelatin. The process may render good services when testing milk or meat products.

L. DE K.

**Application of Dyes to the Recognition and Distinction of Diverse Proteids.** By BOGMOLOW (*Chem. Centr.*, 1894, ii, 855; from *St. Petersb. med. Woch.*, 1894, No. 34).—The following colour reactions are given:—Albumin with corallin, blue-rose. Myosin with methylene-blue and gentian-violet, a blue shade; with methylene-green, a decidedly dark green; with eosin and floxin, a raspberry-red. Peptone with congo, orange-red precipitate; with eosin, methyl-green and safranine, a change of shade without dichroism; with corallin powder, orange-yellow, but no colour with the solution; with floxin, raspberry-coloured flocks. Nucleoalbumin with eosin, orange; with methyl-green, pure green; with gentian-violet, blue. Syntonin with congo, brown; with safranine, yellow; with corallin, reddish-yellow; with methyl-green, green. Alkali albuminate with eosin, rose-violet; with corallin, cherry-violet; with safranine, no change; with congo, a red shade; with floxin, no change. Fibrin becomes coloured by all colouring matters, most feebly with acid magenta. Mucin can, according to Zenoni, be recognised in sputum by mixing the sample on a clock-glass with alcohol and adding safranine, whereon mucin becomes yellow, but albumin (in sputum from pneumonic patients) red. Oxyhæmoglobin crystals from a dog or horse are decolorised by solutions of dye-stuffs in part without change of form, but in part with distortion at the ends, so that they assume a form resembling that of hæmatoidin crystals. Methhæmoglobin and hæmoglobin, on the other hand, are coloured by a whole series of colouring matters. Oxyhæmoglobin, crushed under the cover-glass, is dyed red by rubin, hæmoglobin becoming violet. A. G. B.

**Medico-Legal Detection of Blood Stains.** By FRIEDRICH GANTTER (*Zeit. anal. Chem.*, 1895, 34, 159—160).—It is often of importance to be able to prove that the stains on rusty iron are not due to blood, and this, in consequence of the difficulty of obtaining the usual blood reactions under these conditions, has not hitherto been possible. A highly sensitive reaction is, however, obtained as follows. A small fragment of the rust, placed on a microscope slide on a black ground, is treated with a drop of feebly alkaline water. Any air bubbles which escape, disappear almost instantly, especially on rubbing with a glass rod. On now adding a drop of hydrogen peroxide, numerous bubbles of oxygen are speedily produced, and collect in the form of a delicate froth, surrounded by a ring of clear liquid, the froth remaining permanent for several hours. Stains six months' old give this result as sharply as fresh ones. The non-production of this effect may be regarded as a certain proof of the absence of blood, but the reaction is unfortunately not characteristic for blood, since it is equally produced by pus and other animal products. It affords, however, an admirable means of confirming the presence of hæmin crystals, when, as sometimes happens, the mere microscopic appearance is not sufficiently certain. M. J. S.

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## General and Physical Chemistry.

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**The Constancy of the Calomel Electrode.** By GEORGE W. COGGESHALL (*Zeit. physikal. Chem.*, 1895, **17**, 62—86).—The author prepared a number of calomel electrodes, in order to test their values and constancy at different times. The first set of experiments gave, from time to time, undoubted deviations from a constant value, and the form was slightly altered by placing over the mercury a quantity of sand grains, by which the surface of the calomel was increased and the saturation of the solution more completely ensured. With these cells it was found that the electromotive force during 40 days did not deviate from the normal value by more than 0.0008 volt. Experiments were next performed to test whether the size of the mercury surface affected the constancy of the electrode, the results being in the negative. The time required for the E.M.F. to reach its constant value was in most cases from 30 hours to two days. The effect of slight impurities was found by the use of commercial calomel and mercury, and although the purity of the mercury is of considerable importance, the commercial calomel is only very slightly inferior to the pure compound. It is hence possible to obtain a number of electrodes giving similar results, and the constancy of ordinary calomel electrodes may be regarded as within about 0.001—0.002 volt. The temperature influence was also determined, and the E.M.F. found to increase with the temperature; the coefficient between 0° and 25° being 0.000678 and between 25° and 50°, 0.000647 (volt per degree), whilst the E.M.F. reaches its value in a few hours after the increase of temperature. The absolute value found by Rothmund was 0.561, a number the author considers as probably correct (this vol., ii, 35).

L. M. J.

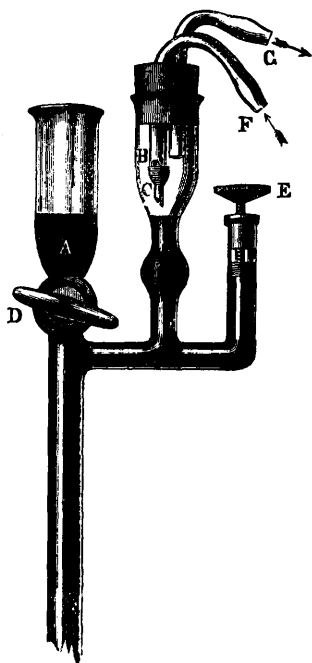
**Electrical Conductivity near the Critical Temperature.** By ADOLFO BARTOLI (*Gazzetta*, 1895, **25**, i, 205—207).—The author has repeated and confirmed his early observations on the electrical conductivity of liquids and gases near the critical temperature, using slightly modified apparatus. Pure benzene has no conductivity either in the liquid or gaseous state, that is, just below and just above the critical temperature. Methyl alcohol and sulphurous anhydride, however, conduct slightly when liquid just below the critical temperature, but lose this feeble conductivity when gaseous just above that temperature.

W. J. P.

**Specific Heat of Hydrogen Peroxide.** By WALTER SPRING (*Zeit. anorg. Chem.*, 1895, **9**, 205—211).—The author has determined the specific heat of solutions of hydrogen peroxide of different strengths, at temperatures from 50—20°, employing the radiation method. A solution containing 71.54 per cent. of hydrogen peroxide has the lowest specific heat, namely, 0.7615. A solution containing 74.54 per cent. gave the specific heat 0.7845, and when the specific heat of hydrogen peroxide is calculated by taking into

account the specific heat of the water present, the number 0.6893 is obtained, and this number varies to a less degree with the temperature than is the case with solutions containing less hydrogen peroxide. Probably a decomposition takes place, and the value obtained represents the specific heat plus the heat formed by the reaction  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ . The smallest value, 0.6208, is obtained with a solution containing 34.25 per cent. of hydrogen peroxide; but this again increases to 0.8065 for a solution containing 30.59 per cent. of hydrogen peroxide; whence the author concludes that, with regard to the specific heat, solutions of hydrogen peroxide behave like an aqueous solution of alcohol, for which the specific heat is greater than the sum of the specific heats of its constituents.

E. C. R.



**Thermostat.** By BERLEMONT (*Bull. Soc. Chim.*, 1895, [3], 13, 228—229).

—The lower part, not shown in the figure, is immersed in the oven, &c. The mercury, on expanding, rises in the middle tube, and cuts off the main supply of gas, enough only to keep the burner alight being allowed to pass through an aperture B, the size of which is regulated by an india-rubber ring C. In setting the apparatus, the mercury is allowed to flow from the middle tube back into the funnel A, until the gas is cut off within 10—15° of the desired temperature, and the adjustment is then completed by means of a screwed piston E. The maximum variation at high temperatures is stated to be 3°. Another form is made to work to 0.2° at temperatures about 35°.

JN. W.

**Solidification of some Carbon Compounds.** By LOUIS BRUNER (*Compt. rend.*, 1895, 120, 914—915).

—Bromal hydrate when it solidifies, does not at once liberate the whole of

its latent heat of fusion, but the action of aqueous potash develops from 2 to 4 Cals. more one hour after solidification than it does some days after solidification. The substance returns gradually to its original condition, and the latent heat of fusion is only slowly liberated, as observed by Berthelot in the case of chloral hydrate.

Thymol and menthol, on the other hand, although pasty after solidification, retain none of their latent heat of fusion.

C. H. B.

**Melting Point of Difficultly Fusible Organic Compounds.** By ARTHUR MICHAEL (*Ber.*, 1895, 28, 1629—1633).—The melting point of many organic substances cannot be determined in the usual

way, either because the substance sublimes before melting, or because it decomposes before the melting point is reached; the latter case being particularly frequent with substances of high melting point. If, however, the substance is brought into a bath already heated very nearly to its melting point, and the temperature of the bath is then rapidly raised, a melting point can often be found. For this purpose, it is best to enclose the substance in a tube sealed at both ends; this tube is best made of hard glass in the case of a substance of very high melting point, and should be not less than 1 mm. in diameter, so as to avoid the influence of capillarity. It is fastened by a spirally wound platinum wire to a glass rod, and is pushed down into the bath, when the latter has reached a suitable temperature. For temperatures up to 300° a bath of sulphuric acid was used; for those between 300—400° a bath of paraffin, of which about one-third has first been distilled off; the boiling point of the residue falls with use, however. For temperatures of 400—450° an air bath, kept rapidly stirred, was used, and heated in a bath of fusible metal; the substance was brought just below the level of the latter, and lighted by a reflected ray of sunlight.

In one or other of the above ways, the following melting points were determined. They varied somewhat with the time and manner of heating, and the experiment had often to be repeated several times in order to get an accurate estimation. Fumaric acid, 287—288°. Dibromosuccinic acid, 260—261°. Mellitic acid, 286—288°. Chlor-anilic acid, 283—284°. Asparagine, 234—235°. Aspartic acid, 270—280° (not quite all melted). Theobromine, 329—330°. Oxamide, 417—419°. Indigo blue, 390—392°. C. F. B.

**The Determination of Boiling Points by the Dynamical Method.** By GEORG W. A. KAHLBAUM (*Ber.*, 1895, **28**, 1675—1681).—In a recent abstract (*Ann. Phys. Chem.*, *Beibl.*, 1895, **19**, 321), C. G. Schmidt states that the boiling points of liquids determined by the author by the dynamical method in many cases do not represent the normal boiling point but the boiling point of the superheated liquid. In the present paper, the author adduces a large number of new figures to prove that Schmidt's statement is incorrect, and that the numbers previously given are in reality the normal boiling points.

H. G. C.

**Critical Temperature of Hydrogen.** By LADISLAUS NATANSON (*Zeit. physikal. Chem.*, 1895, **17**, 43—48, and *Phil. Mag.*, **40**, 272—282).—From the equation  $pv/p_c v_c = Kt/t_c$  (where  $p_c$ ,  $v_c$ , and  $t_c$  are the critical values of the pressure, volume, and temperature) is deducible, the relation  $t_c = AMp_c v_c$ , where  $M$  is the molecular weight and  $A$  a constant for all gases. The value of this constant for carbonic anhydride is  $5.4344 \times 10^{-7}$  in absolute units, the values for other gases giving satisfactory agreement. Using this value, the author calculates the critical densities of oxygen, argon, carbonic oxide, nitrous oxide, methane, ethane, and propane, the last three giving the numbers 0.202, 0.216, and 0.230 respectively. For hydrogen, use is made of Van der Waal's equation, and the deducible relatives  $v_c = 3b$ ;  $t_c/p_c = 8b/R$ , from which if the value  $b = 0.00070$  is taken, the critical volume of hydrogen is obtained as 23.45 (cc/gm), and if Olzewski's value of



$\text{Hg}_2 \text{ liq.} + \text{S sol.} + \text{O}_1 \text{ gas} = \text{Hg}_2\text{SO}_4 \text{ sol.}$	develops	+175.0	Cals.
$\text{Hg}_2 \text{ liq.} + \text{N}_2 \text{ gas} + \text{O}_6 \text{ gas} + \text{H}_2\text{O liq.} =$			
$\text{Hg}_2(\text{NO}_3)_2, 2\text{H}_2\text{O sol.} \dots\dots\dots$	„	+69.4	„
$\text{Hg}_2 \text{ liq.} + \text{C}_4 \text{ (diamond)} + \text{H}_6 \text{ gas} + \text{O}_1$			
$\text{gas} = \text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2) \text{ sol.} \dots\dots\dots$	„	+202.1	„
		C. H. B.	

**Heats of Formation of Mercurous Chloride, Bromide, Iodide, and Oxide.** By RAOUL VARET (*Compt. rend.*, 1895, **120**, 1054—1057).—The methods employed were in general the same as in the case of the acetate, nitrate, and sulphate (preceding abstract). The heat of formation of the oxide was determined by the action of alkali hydroxides on the chloride, nitrate, and sulphate. The results are as follows.

$\text{Hg}_2 \text{ liq.} + \text{Cl}_2 \text{ gas} = \text{Hg}_2\text{Cl}_2 \text{ sol.} \dots\dots\dots$	develops	+62.63	Cals.
$\text{Hg}_2 \text{ liq.} + \text{Br}_2 \text{ liq.} = \text{Hg}_2\text{Br}_2 \text{ sol.} \dots\dots\dots$	„	+49.05	„
$\text{Hg}_2 \text{ liq.} + \text{I}_2 \text{ sol.} = \text{Hg}_2\text{I}_2 \text{ sol., yellow}$			
$\text{amorphous.} \dots\dots\dots$	„	+28.85	„
$\text{Hg}_2 \text{ liq.} + \text{I}_2 \text{ sol.} = \text{Hg}_2\text{I}_2 \text{ sol., yellow-}$			
$\text{green amorphous} \dots\dots\dots$	„	+28.55	„
$\text{Hg}_2 \text{ liq.} + \text{O gas} = \text{Hg}_2\text{O sol.} \dots\dots\dots$	„	+22.17	„
		C. H. B.	

**Nature and Cause of Osmotic Pressure.** By ETTORE MOLINARI (*Gazzetta*, 1895, **25**, i, 190—205).—The author gives a brief outline of our present knowledge respecting the nature and cause of osmotic pressure, and then endeavours to explain the phenomena involved, by the following analogy. Suppose a vessel containing under unit pressure a gas A, which cannot penetrate or diffuse through the walls, to be immersed in an atmosphere of a second gas B, also under unit pressure, which, however, has the property of diffusing through the walls of the vessel; the gas B will diffuse into and out of the vessel, until at length as many molecules of B will leave the vessel as enter it in unit time. When this stage is reached, equilibrium is, of course, established between the inside and outside of the vessel, although the total pressure inside the vessel, being the sum of the partial pressures of A and B, is greater than the pressure on the exterior. The behaviour of a sugar solution in a Pfeiffer's cell is quite similar to this, the sugar and solvent taking the places of the gases A and B respectively; the author further argues that the sugar molecules, which are in a state resembling that of a gas, check the free exit of the water molecules to an extent proportional to the concentration of the solution, so that the osmotic pressure is also proportional to the latter.

W. J. P.

**Determination of Isosmotic Concentrations.** By S. G. HEDIN (*Zeit. physikal. Chem.*, 1895, **17**, 164—170).—The author has for many years used a method and apparatus similar to that described by Köppe (this vol., ii, 208). He obtained also the same general results as Köppe, and gives a table of his own numbers for the isosmotic concentrations of cane sugar; sulphates of potassium, sodium, and mag-



nesium; nitrates of potassium, sodium, calcium, strontium, and barium; chlorides of sodium, potassium, calcium, and barium; bromides and acetates of sodium and potassium; sodium phosphate, potassium tartrate, and potassium ferrocyanide. These numbers are compared with those of Köppe, De Vries, Hamburger, Raoult, Arrhenius, Kohlrausch, van't Hoff and Reicher, and Gregory. They are in general higher than those of the three first named observers, but agree better with the results obtained by the freezing point and conductivity methods. The most notable differences are for sodium phosphate (3.12, Köppe, 2.24) and potassium ferrocyanide (2.53, Köppe, 1.72). The method is, he considers, available for a large number of compounds, but not for ammoniacal salts, acids, alkalis, or alkali carbonates.

L. M. J.

### **Increase of Solubility by the Addition of Non-electrolytes.**

By HEINRICH GOLDSCHMIDT (*Zeit. physikal. Chem.*, 1895, **17**, 145—163).—The solubility of an anhydrous compound is affected to only a slight extent, if at all, by the addition of a non-electrolyte. As, however, this addition lowers the transition point from a hydrated to an anhydrous salt, it must in general cause an increase of solubility of the former, and an expression for this increase is theoretically deduced, it being independent of the nature of the non-electrolyte. This conclusion, and the expression, is tested by experiments on the solubility of sodium paranitrophenoxide in pure water, and in equimolecular solutions of carbamide, glycerol, acetone, ethylic cyanide, methylic cyanide, and urethane. The compound crystallises in two forms, the first with  $2\text{H}_2\text{O}$ , the other with  $4\text{H}_2\text{O}$ . The transition temperature was found by the dilatometric method to be  $36^\circ$ , and by the solubility method,  $35.78^\circ$ . Each non-electrolyte caused an increase in solubility of both hydrates, the molecular increase being approximately equal for all the compounds except urethane. Ethylic alcohol caused practically no alteration of the solubility. The lowering of the transition point is calculated according to the theoretical deductions to be  $2.09^\circ$ . The solubility experiments lead to the following results. Urea,  $2.36^\circ$ ; glycerol,  $1.91^\circ$ ; acetone,  $1.67^\circ$ . The agreement between the theory and the experiments is further tested by the comparison of the calculated and found values for the ratio of the molecular increases in solubility of the two hydrates, the results being carbamide, 1.017; glycerol, 1.019; acetone, 1.022; urethane, 1.015; calculated, 1.022.

L. M. J.

**The Determination of Molecular Weights.** By ERNST BECKMANN and AUGUST STOCK (*Zeit. physikal. Chem.*, 1895, **17**, 107—135; see this vol., ii, 154).—As values varying from  $I_1$  to  $I_2$  had been obtained for the molecular weight of iodine in solution by different observers, fresh determinations were made by the authors. The first set of experiments were made by the freezing point method, and gave the following results.

Solvent.	Colour of solution.	Mol. weight.
Benzene .....	red	355
Paraxylene .....	red	256
Ethylene bromide.....	red	244
Bromoform .....	red	276
Naphthalene .....	red	245
Acetic acid.....	brown	256
Urethane .....	brown	256

With the exception of that in benzene, therefore, all the numbers correspond with the formula  $I_2$ . The cause of the abnormal result in benzene solutions was afterwards investigated, and the authors consider that a solid solution is probably formed. Experiments with bromoform and iodine in solution were therefore performed, and from the analysis of the precipitated crystals the quantity of iodine present as a solid solution is estimated. Corrections applied on this account lead to the value 228 for the molecular weight of iodine in benzene solutions.

The next series of experiments were made by the boiling point method, but the ordinary formula for the estimation of the molecular weight cannot be used, owing to the volatility of the iodine. A formula applicable is therefore deduced, in which corrections for the iodine volatilised are applied. The molecular weights obtained thus are as follows.

Solvent.	Colour of solution.	Mol. weight.
Chloroform .....	violet	229
Ethylenic chloride.....	red	212
Benzene.....	red	244
Ethylic alcohol .....	brown	235
Methylic alcohol.....	brown	207
Methylal .....	brown	226
Acetone.....	brown	211
Carbon tetrachloride.....	violet	235

Experiments were also made on the effect of lead and mercury on solutions of iodine in chloroform, when the iodine is almost completely precipitated as iodides, chiefly iodide of mercury, which, however, slowly reacts with the lead. The solubility of mercuric iodide in various solvents is also recorded, and a short note added on the results of Krüss and Thiele (*Abstr.*, 1894, ii, 415), and also on Behrend's experiments on the picrates of phenanthrene and anthracene, which the author considers do not necessitate the existence of molecular complexes (*Abstr.*, 1892, 1385). L. M. J.

**Physical Properties of Solutions of Lithium Chloride in Amylic Alcohol.** By LAUNCELOT N. ANDREWS and CARL ENDE (*Zeit. physikal. Chem.*, 1895, 17, 136—144).—The authors determined the viscosity, specific refraction, conductivity, and dissociation coefficient for solutions of lithium chloride in amylic alcohol at 17 concentrations, varying from 0.537 to 4096 litres per gram mol., the results being recorded in tables. Curves are also drawn, showing the varia-

tion with dilution in the case of the conductivity, refraction, and dissociation. The molecular weight was also determined by the boiling point method, the value being 71.5 in the concentrated solutions, but falling to 40 by sufficient dilution, owing probably to the presence of  $\text{Li}_2\text{Cl}_2$ , or other aggregates, in the concentrated solutions.

L. M. J.

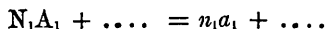
**Formation of Crystals at the bottom of a Solution heavier than themselves.** By PAUL E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, 120, 859—860).—The author has previously discussed cases in which certain substances crystallise at the surface of solutions lighter than themselves, the substances contracting on crystallising from their highly saturated solutions and expanding when they dissolve in liquids highly charged with certain other substances (*Compt. rend.*, 1895, 120, 539). It would seem that substances which expand notably when they crystallise from highly saturated solutions, or which contract on dissolving in liquids charged with certain other substances, might crystallise at the bottom of liquids heavier than themselves. The phenomenon can, in fact, be observed with hydrated sodium sulphate and with ice.

If crystals of the hydrate  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  are allowed to float on the surface of a solution of sodium iodide saturated with sodium sulphate, and with a sp. gr. somewhat higher than the sodium sulphate crystals, after a few days the crystals of the sulphate collect at the bottom of the vessel round a fragment of the solid previously fixed there.

For ice, a solution of ammonia must be used of such strength that a fragment of ice neither increases in it nor melts at  $-3.5^\circ$ . Fragments of ice are allowed to float on the liquid, and a fragment is fixed to the bottom of the vessel, the temperature being kept at  $-3.75^\circ$  to  $-3.25^\circ$ , but never falling to  $-4.0^\circ$  nor rising to  $-3.0^\circ$ . After some hours, the ice has passed to the bottom of the liquid.

C. H. B.

**Law of Mass Action.** By JOSEPH E. TREYOR (*Amer. Chem. J.*, 1895, 17, 372—374).—The author seeks to bring the derivation of the law of mass action from the principles of thermodynamics into a more simple and general form. The law has hitherto found application only in cases in which the free energy of a change in concentration is proportional to the absolute temperature at which the change occurs, and the well-known relation  $pv = RT$  follows. The letters denote successively the actual pressure, the molecular volume, the gas-constant, and the absolute temperature. Let a chemical equilibrium be established between the initial components  $A_1, A_2$ , &c., and the products  $a_1, a_2$ , &c., which they unite to form; let the above relation hold for all constituents, and the equilibrium be represented by the chemical equation



At equilibrium, the free energy  $F$  developable by this system must be a maximum, so for a virtual displacement in the positive direction of change

$$\delta F = 0$$

$$\delta F \equiv \sum n_i v_i \delta p - \sum N_i V_i \delta P = 0,$$

the two terms of the left-hand member of the equation being summated over all the initial components (capitals) and their products (small letters) respectively. Substituting the molecular concentrations  $c$  and  $C$  in the state of equilibrium,

$$\delta F \equiv RT(\sum n \delta \log c - \sum N \delta \log C) = 0.$$

The work value of the process, the limiting value of  $F$  for the change considered as occurring isothermally at its equilibrium, is obtained by integration of this virtual change over the entire transformation of  $n_i$ , &c., mols.,

$$F = RT \int (\sum \delta \log c^n - \sum \delta \log C^N),$$

the constant of integration disappearing from the definite integral. This becomes

$$F = RT \log K,$$

when the change is conducted in the positive direction, and  $K$  is set for the ratio  $\Pi c^n / \Pi C^N$ . And since  $F$  must be constant for a given isothermal change, this ratio must be constant also, which is the law of mass action.

H. C.

**The Velocity of Formation of Amines and of Alkyl Ammonium Salts.** By N. MENSCHUTKIN (*Ber.*, 1895, **28**, 1398—1407).—The alkyl bromide (1 mol.) and the amine (2 mols.) were heated with benzene (15 vols. to one of the mixture) at 100° in sealed tubes, and the amount of hydrobromide formed was estimated by titration with silver solution according to Mohr's method. The equation  $dx/dt = (A - x)(B - x)c$  represents the reaction, and as  $A = 2B$ ,

$$c = \log \frac{A - x/2}{A - x} \cdot \frac{1}{t}.$$

The following are the results.

#### I.

$c \times 10^6$	$c \times 10^6$
NHMe <sub>2</sub> + MeBr = 59954	NH <sub>2</sub> Pr + MeBr = 15215
NMe <sub>3</sub> + MeBr = 47437	NHPr <sub>2</sub> + MeBr = 10264
NH <sub>2</sub> Me + MeBr = 31910	NH <sub>3</sub> + MeBr = 5471
NH <sub>2</sub> Et + MeBr = 19377	NEt <sub>3</sub> + MeBr = 5380
NHEt <sub>2</sub> + MeBr = 16886	

#### II.

$c \times 10^6$	$c \times 10^6$
NMe <sub>3</sub> + C <sub>3</sub> H <sub>5</sub> Br = 34263	NH <sub>2</sub> Pr + C <sub>3</sub> H <sub>5</sub> Br = 3783
NHMe <sub>2</sub> + C <sub>3</sub> H <sub>5</sub> Br = 30833	NHPr <sub>2</sub> + C <sub>3</sub> H <sub>5</sub> Br = 2910
NH <sub>2</sub> Me + C <sub>3</sub> H <sub>5</sub> Br = 8302	NH <sub>3</sub> + C <sub>3</sub> H <sub>5</sub> Br = 1380
NH <sub>2</sub> Et + C <sub>3</sub> H <sub>5</sub> Br = 3807	NEt <sub>3</sub> + C <sub>3</sub> H <sub>5</sub> Br = 757

## III.

$c \times 10^6.$	$c \times 10^3.$
$\text{NHMe}_2 + \text{EtBr} = 1534$	$\text{NHEt}_2 + \text{EtBr} = 182$
$\text{NMe}_3 + \text{EtBr} = 1053$	$\text{NH}_3 + \text{EtBr} = 124$
$\text{NH}_2\text{Me} + \text{EtBr} = 490$	$\text{NHPr}_2 + \text{EtBr} = 101$
$\text{NH}_2\text{Et} + \text{EtBr} = 214$	$\text{NEt}_3 + \text{EtBr} = 30$
$\text{NH}_2\text{Pr} + \text{EtBr} = 184$	

## IV.

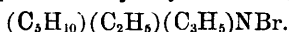
$c \times 10^6.$	$c \times 10^6.$
$\text{NH}_2\text{Et} + \text{PrBr} = 65$	$\text{NHPr}_2 + \text{PrBr} = 21$
$\text{NH}_2\text{Pr} + \text{PrBr} = 60$	$\text{NPr}_3 + \text{PrBr} = 0.5$
$\text{NH}_3 + \text{PrBr} = 44$	

With the exception of ammonia, which appears to be anomalous in its position, the amines follow the same order in each series, the di- and tri-methylamine being by far the strongest bases.

The author shows that the velocity of formation of a mixed amine depends on the order in which the different alkylic groups are introduced. Thus, with  $\text{NHMeEt}$ —

- $c \times 10^6.$
- (1.)  $2\text{NH}_2\text{Me} + \text{EtBr} = \text{NHMeEt} + \text{NH}_2\text{Me}, \text{HBr} = 490$   
 (2.)  $2\text{NH}_2\text{Et} + \text{MeBr} = \text{NHMeEt} + \text{NH}_2\text{Et}, \text{HBr} = 19377$

and similarly with piperidineethylallyl bromide,



It is further shown in the latter case that the final product itself is independent of the order in which the alkylic groups are introduced.

From the tables, it follows that the displacement of one of the hydrogen atoms of ammonia by (1) a methyl group increases the velocity to a considerable extent, namely, 25439; (2) an ethyl group only to a slight extent, namely, 90; and (3) a propyl group does not appreciably increase the velocity. It is further shown that the capability of nitrogen compounds to form derivatives in which the nitrogen atom is quinquivalent depends largely on the nature of the elements or groups to which the nitrogen atom is already united.

J. J. S.

**Determination of the Affinities of Acids colorimetrically by means of Potassium Dichromate.** By J. H. KASTLE and B. C. KEISER (*Amer. Chem. J.*, 1895, 17, 443—449).—This method depends on the fact that potassium dichromate is converted into normal chromate by the alkali salts of feeble acids, the extent of the change being indicated by the variation of the colour of the dichromate towards that of the chromate. Since it is impossible to prepare a normal solution of potassium dichromate, and since the addition of a decinormal solution of an alkali salt to a decinormal solution of the dichromate causes too slight a change of colour for accurate measurement, it was necessary to use decinormal dichromate and normal alkali salt. One c.c. of the N/10 dichromate is mixed in a thin glass cylinder (30 c.c. capacity) with 10 c.c., or other suitable quantity, of

the N alkali salt of the acid whose affinity is to be determined. In a similar cylinder, 1 c.c. of the N/10 dichromate is diluted with water to nearly the same volume, the equality being perfected by the addition of N/10 soda solution, added drop by drop until the colour of the liquids in the two cylinders is identical. The method of calculating a number to express the affinity of the acid when that of potassium dichromate is called 1 may be understood from the following example.

1.5 c.c. N/10 caustic soda was required to produce the same colour as 10 c.c. of N sodium acetate solution; this quantity of NaOH is equivalent to 0.0123 gram of  $\text{NaC}_2\text{H}_3\text{O}_2$ , which is, therefore, the quantity of sodium acetate which has been decomposed by the dichromate; calculated to a percentage on the sodium acetate used, the number becomes 1.5, and if the affinity of the dichromate be called 1, that of acetic acid under the conditions of this experiment is  $1 \times \frac{100 - 1.5}{1.5} = 65.6$ .

The numbers obtained in this way, at different degrees of dilution, are given hereunder.

	c.c. of normal solution.				
	5.	7.	10.	15.	20.
Acetic .....	44.0	53	65.6	90.7	116
Formic .....	—	—	153.0	—	199
Butyric .....	30.2	39	—	—	—
Benzoic .....	—	—	124.0	—	—
Crotonic .....	51.6	—	74.6	102.0	128
Monobromacetic ....	—	—	399.0	—	665

It will be noticed that essentially the same relation exists between the numbers obtained for one quantity of the several salts used and those obtained for other quantities.

It is shown in a table that the authors' results give figures which bear a ratio to each other similar to that which exists between the numbers obtained by other methods of investigating relative affinity.

A. G. B.

**Apparatus for Fractional Distillation.** By PAUL MONNET (*Bull. Soc. Chim.*, 1895, [3], 13, 108—114).—A column of beads, about 135—140 cm. high, and 28—35 mm. in diameter, resembling Hempel's well-known device. The beads may be of glass, but consist preferably of various sizes of lead shot, graduated from large below to small above, and separated by copper gauze diaphragms to facilitate removal for cleaning. By the use of this apparatus, 90 per cent. alcohol can be separated from a comparatively small amount—300 c.c.—of 50 per cent. spirit in one operation, and such mixtures as benzene and toluene, and aniline and orthotoluidine, can be satisfactorily and completely resolved into their constituents. JN. W.

## Inorganic Chemistry.

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**Absorption of Hydrogen by Palladium.** By C. HOITSEMA (*Zeit. physikal. Chem.*, 1895, **17**, 1—42).—The researches of Troost and Hauteville had led those chemists to the conclusion that the absorption of hydrogen by palladium is accompanied by the formation of a compound represented by  $\text{Pd}_2\text{H}$ . The author undertook researches to further investigate this question, and, after a short consideration of the conditions of equilibrium between a solid and gas, gives a description of the apparatus which was used in his experiments. The quantity of hydrogen absorbed by a known weight of the metal, and the pressure of the gas, were determined with varying quantities of hydrogen at every 10 degrees between  $20^\circ$  and  $200^\circ$ , and from these results the isothermal curves are drawn with pressure ordinates, and the atomic ratios of the absorbed hydrogen and the palladium, as abscissæ. Some similar numbers, due to Roozeboom, but previously unpublished, are also added. The curves show the same essential features, and, although small differences are observed to follow the use of different varieties of metal, the agreement between the results is very satisfactory; the pressure at first increases with the hydrogen content, then a second position is reached where the curve is nearly horizontal, the pressure increasing only very slowly, and in the final portion the pressure again rapidly rises. The length of the central portion of the curve diminishes as the temperature rises, but had not disappeared in any of the experiments. There are no sudden breaks, the three portions being continuous. The author considers the slow increase of pressure in the middle part to be an essential feature, and not due to accidental impurities, &c., and the curves do not support the supposition of the formation of the compound  $\text{Pd}_2\text{H}$ . He considers they are better explained by the assumption of two non-miscible solid solutions, and further draws attention to the similarity between these and liquefaction curves, so that the experiments could be explained by the supposition that a kind of liquefaction of hydrogen takes place, for which the critical temperature is far higher than that of hydrogen in ordinary conditions. The molecular state of the gas is also calculated, and, though at first represented by  $\text{H}_2$ , the gas appears above  $100^\circ$  to be monatomic, the expression  $pr/\sqrt{p}$  having an approximately constant value.

L. M. J.

**Argon and Fluorine.** By HENRI MOISSAN (*Compt. rend.*, 1895, **120**, 966—968).—Titanium, boron, lithium, and uranium are not affected when heated in argon.

Argon and fluorine do not combine either at the ordinary temperature or under the influence of an electric spark. C. H. B.

**Combustion in Nitrogen.** By FRIEDRICH EMICH (*Ber.*, 1895, **23**, 1585).—The author points out that the combustion of titanium in

nitrogen described by Moissan (this vol., ii, 272), is not the first instance of the kind, since Prelinger (this vol., ii, 16) has previously described the similar behaviour of metallic manganese. A. H.

**Thiohypophosphates.** By L. FERRAND (*Bull. Soc. Chim.*, 1895, [3], 13, 115—117).—Zinc, cadmium, and nickel thiohypophosphates can be prepared by Friedel's method, namely, by heating the metal or its sulphide to redness for 40 hours or more with sulphur and phosphorus in sealed tubes imbedded in iron tubes filled with sand. The zinc salt,  $\text{Zn}_2\text{P}_2\text{S}_6$ , crystallises in small, transparent, yellow plates, apparently hexagonal; it is insoluble in cold water, and in hydrochloric or nitric acids, but is partially decomposed by boiling water, and entirely by nitrohydrochloric acid; sp. gr. = 2.2. The cadmium salt forms orange-yellow, biaxial crystals. The nickel salt, prepared from the sulphide, forms very brilliant, grey, hexagonal crystals, and is scarcely attacked by nitrohydrochloric acid; sp. gr. = 2.4.

JN. W.

**New Method for Preparing Alkali Metals.** By NICOLAI N. BÉKÉTOFF and SCHERRATSCHIEFF (*Chem. Centr.*, 1895, i, 145; from *Bul. Acad. St. Pétersb.*, 1894, [5], i).—The alkali metals may be prepared by Winkler's process of distilling their aluminates with magnesium; the authors prepare metallic caesium by removing the sulphuric acid from caesium alum by baryta, adding aluminium hydroxide to the filtered solution, evaporating in an iron or nickel dish, and heating the residue to redness. The product, which is scarcely hygroscopic, is distilled from an iron tube with the requisite weight of magnesium, the caesium being collected in a glass vessel.

Caesium thus obtained has the density 2.366, not 1.83 as found by Settler; its atomic volume is consequently 56, a much more probable value than the older one of 75.

W. J. P.

**Acid Fluorides of Potassium and Silver.** By ANTOINE GUNTZ (*Bull. Soc. Chim.*, 1895, [3], 13, 114—115).—The heat of formation of ordinary potassium hydrogen fluoride (solid) from its proximate constituents (solid and gaseous) is 21.1 cals. The heats of dissolution of the di- and tri-hydrogen fluorides,  $\text{KF}\cdot 2\text{HF}$ , and  $\text{KF}\cdot 3\text{HF}$ , are  $-8.0$  and  $-8.6$  cals. respectively, whence the heats of formation of these latter (solid) from potassium fluoride (solid) and hydrogen fluoride (liquid) are  $+6.5$  and  $+11.6$  cals. The heat liberated by the addition of 1 mol. of hydrogen fluoride (liquid) to potassium fluoride and the mono- and di-hydrogen salts respectively (solid) is  $+13.9$ ,  $+6.5$ , and  $+3.1$  cals. The stability of these double fluorides thus decreases on ascending the series. Cryoscopic determinations with the two higher salts show that they are almost completely dissociated in aqueous solution.

*Silver trihydrogen fluoride*,  $\text{AgF}\cdot 3\text{HF}$ , is obtained in colourless, fuming crystals by dissolving silver fluoride, or, more conveniently, silver subfluoride in aqueous hydrofluoric acid; the action is strongly exothermic, the heat of formation of the salt being about  $+2.0$  cals. The double fluoride is very unstable, as its vapour pressure is con-



siderable at ordinary temperatures, and on exposing it to a current of dry air, even at  $0^{\circ}$ , it is converted into the monhydrogen fluoride.

JN. W.

**An Alcoholate of Calcium Bromide.** By FERDINAND ROQUES (*J. Pharm.*, 1895, [6], 1, 301—303).—Fused calcium bromide is powdered and placed, whilst still hot, in a flask and covered with pure absolute alcohol. Much heat is developed, and a small quantity of free lime separates. The solution is diluted with some more alcohol and filtered into a dish through a filter large enough to hold all the liquid at once, and the whole is then placed under a large desiccator containing sulphuric acid.

In the author's experiment, the crystals had formed after a lapse of four months. They were quickly dried between filter-paper, and, on analysis, gave figures corresponding with the formula  $\text{CaBr}_2 \cdot 3\text{C}_2\text{H}_5\text{O}$ . The crystals are very large, rhomboid tables, easily cleavable, very hygroscopic, and readily take fire. When calcined to remove the alcohol, they are partly decomposed into free lime, ethylic bromide, and hydrogen bromide.

L. DE K.

**Purification of Zinc.** By FRANZ MYLIUS and OTTO FROMM (*Ber.*, 1895, 28, 1563—1575, and *Zeit. anorg. Chem.*, 1895, 9, 144—177).—Ordinary purified zinc contains lead, iron, and cadmium in amounts varying from 2 to 111 parts per 100,000 according to the quality of the sample. The purest specimens which were purchased by the authors, and were called "specially pure," contained 5 parts of lead, 16 of cadmium, and 1.4 of iron per 100,000. Zinc can readily be freed from lead and cadmium by crystallisation, these impurities remaining in the mother liquor, but not from iron, which tends to accumulate in the crystals. Is is best purified by electrolysis in basic zinc sulphate solution. The process must be frequently repeated, the spongy mass which is obtained at the cathode being formed into the anode for the next operation. The final product is melted in a porcelain crucible and distilled in a vacuum. It then contains less than 1 part of impurity per 100,000; compact zinc, obtained by the use of platinum electrodes, contains about 1/100 per cent. of platinum.

A. H.

**Synthesis of Minerals and analogous Metallic Compounds by Crystallisation from Molten Metals.** By FRIEDRICH ROESSLER (*Zeit. anorg. Chem.*, 1895, 9, 31—77).—Silver sulphide in varying proportions was dissolved in silver under borax and allowed to cool slowly. The cornets obtained have a coarser fracture and darker colour the more silver sulphide they contain. With 20 per cent. and more of silver sulphide the cornet separates into two layers, and the layer of silver contains dark particles of sulphide. When the cornets are treated with dilute nitric acid, the silver sulphide is obtained in lustrous, black particles. A cornet containing 2 per cent. of silver sulphide, when etched with dilute nitric acid, showed the sulphide arranged in lines of rounded particles. The silver sulphide, which has a lower melting point than silver, is fluid when it separates from the solution, so that it cannot be obtained crystalline by this method. Silver selenide dissolved in silver behaves in the same way as the

sulphide. The sulphide and selenide, although they do not separate in crystals, have the same composition and physical properties as the naturally occurring minerals.

Sulphide of lead crystallises from lead in beautiful cubes, sometimes arranged in steps or needles; when treated for some time even with dilute nitric acid, it is partially decomposed, and the crystals are best separated from the matrix by electrolysis, using a solution of lead acetate, sodium acetate, and acetic acid in water, and a current density of 0.2—0.3 ampère. Lead selenide also crystallises well from lead in beautiful cubes or aggregates of cubes; the crystals are best separated from the matrix by electrolysis, but even then it is difficult to obtain them pure.

When sulphur is melted with bismuth under borax, a dark coloured dross is formed containing sodium sulphide. Bismuth sulphide may be easily crystallised by dissolving the previously prepared compound in bismuth and allowing the solution to cool. It dissolves in bismuth in all proportions, crystallises in long needles identical with the natural compound, and is easily separated from the matrix by dilute nitric acid. Bismuth selenide crystallises from bismuth in rhombohedral tablets or regular octahedra; the crystals are not identical with those of natural bismuth selenide; they are difficult to separate from the matrix, and gave on analysis numbers agreeing with the composition  $\text{Bi}_2\text{Se}$ .

Silver bismuth sulphide,  $\text{Ag}_2\text{S}, \text{Bi}_2\text{S}_3$ , is obtained when silver sulphide is dissolved in bismuth, and the cornet then treated with dilute nitric acid. It crystallises in beautiful groups of octahedra, has the same composition as the natural mineral, but not the same crystalline form. Silver selenide crystallises from bismuth in four-sided columns.

Cuprous sulphide and selenide crystallise from lead, the former in beautiful octahedra, the latter in reddish-yellow and steel-blue octahedra and feathery aggregates. The author was unable to prepare zorgite,  $\text{PbSe}, \text{Cu}_2\text{Se}$ , or emplectite,  $\text{Cu}_2\text{S}, \text{Bi}_2\text{S}_3$ .

Palladium sulphide,  $\text{Pd}_2\text{S}$ , is obtained by melting palladium ammoniochloride with sulphur under borax. It is a greyish-yellow, crystalline mass, and so hard that it is scarcely scratched by steel. When melted with palladium under glass, it yields a cornet, which, after treatment with concentrated nitric acid, yielded irregular, grey, metallic particles very similar to those of the platinum earths.

Palladium selenide,  $\text{PdSe}$ , obtained in a similar manner to the sulphide, melts at a lower temperature than silver, and is completely soluble in aqua regia. When melted with palladium, it yields grey, irregular particles similar to the sulphide. These particles on analysis gave numbers agreeing with the composition  $\text{Pd}_4\text{Se}$ .

The author was unable to prepare platinum sulphide by melting together platinum and sulphur.

Platinum selenide,  $\text{PtSe}$ , is easily obtained by melting platinum and selenium together under borax. A dark grey, lustrous cornet is obtained which breaks into lustrous plates on gently hammering it. When melted with platinum, it forms bright particles.

*Antimony platinum*,  $\text{PtSb}_2$ , is obtained by melting antimony (400

grams) with platinum powder (10 grams) and then dissolving the matrix in a mixture of equal parts of nitric acid and tartaric acid. It crystallises in dark grey, lustrous cubes and octahedra, and is very hard and brittle.

*Bismuth platinum*,  $\text{PtBi}_2$ , obtained in a similar way to the preceding compound, crystallises in dark grey, brown, and blue plates, and is very brittle.

*Antimony palladium*,  $\text{PdSb}_2$ , was not obtained crystalline. On treating the cornet with acid, small grey particles were obtained which had evidently been attacked by the acid.

*Bismuth palladium*,  $\text{PdBi}_2$ , crystallises in small, interlacing needles.

*Bismuth gold*,  $\text{Au}_3\text{Bi}$ , is obtained by dissolving gold in a large excess of bismuth. It crystallises in very small, grey crystals, sometimes in minute octahedra.

*Antimony gold* crystallises in small, grey crystals which turn red or bronze colour when dissolved out with acid. It has probably the composition  $\text{Au}_3\text{Sb}$ .

E. C. R.

### Action of Halogen Compounds of Phosphorus on Copper.

By A. GRANGER (*Compt. rend.*, 1895, 120, 923—924).—When copper is heated at  $300^\circ$  in sealed tubes with phosphorus trichloride or tribromide, copper phosphide is formed, but cannot be separated from the cupric chloride or bromide. With phosphorus biiodide, under similar conditions, the metal is only imperfectly attacked.

When carbonic anhydride charged with vapour of phosphorus trichloride, tribromide, or biiodide is passed over gently heated copper, the biphosphide,  $\text{CuP}_2$ , is obtained as a crystalline solid with a colour and lustre resembling that of silicon. It is readily attacked by chlorine, bromine, or nitric acid, and more slowly by hydrochloric acid. When heated out of contact with air, it yields cupric phosphide and phosphorus; heated in presence of air, it oxidises, and when mixed with oxidising agents such as potassium chlorate, it detonates when struck.

Phosphorus trifluoride, under similar conditions, yields the phosphide,  $\text{Cu}_3\text{P}_2$ , previously described (*Abstr.*, 1892, 410).

C. H. B.

**Copper-Aluminium Alloys: a Correction.** By HENRI L. LE CHATELIER (*Compt. rend.*, 1895, 120, 1050—1051).—The alloy described as  $\text{AlCu}$  (this vol., ii, 351), and said to be superficially attacked by the potash solution, has really been more or less completely attacked. The definite compound contains a higher proportion of aluminium, and although the author's researches on the fusibility of copper-aluminium alloys indicate the existence of two definite compounds,  $\text{Al}_2\text{Cu}$  and  $\text{AlCu}_3$ , this conclusion requires confirmation by other methods.

The peculiar manner in which aluminium alloys undergo alteration may have led to many erroneous conclusions. In one case, an ingot obtained by fusing equal weights of copper and aluminium was left for 24 hours in a sodium chloride solution containing lead chloride, in order to dissolve the free aluminium. There seemed to be no action, and the ingot retained its original appearance, but after being

washed, dried, and exposed to the air for about 12 hours, it changed spontaneously to a small heap of blackish powder, whereas another piece of the same alloy, which had not been treated with sodium chloride solution, remained quite unaltered for at least a month.

C. H. B.

**Hydrolysis of Aqueous Solutions of Mercuric Chloride.** By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1895, 9, 178—189).—When a rod of marble is allowed to remain in an aqueous solution of mercuric chloride, carbonic anhydride is formed by the action of the acid liberated by the hydrolysis of the mercuric chloride. At the same time crystalline basic salts are deposited. The composition of these salts depends on the temperature, concentration of the solution, and the ratio of the area of the rod of marble to the bulk of solution. An aqueous solution of mercuric bromide behaves in the same way, but less basic salts are formed. Mercuric iodide is not hydrolysed at the ordinary temperature, and at 170° only a very small quantity of basic salt is formed. The salt  $\text{HgCl}_2 \cdot 3\text{HgO}$  is obtained by heating a 5 per cent. solution of mercuric chloride for one month at 80°; the salt  $\text{HgCl}_2 \cdot 4\text{HgO}$  by heating the solution at 100°. The salt  $\text{HgCl}_2 \cdot 4\text{HgO}$  is formed in very small quantity together with the salt  $2\text{HgCl}_2 \cdot \text{HgO}$  at the ordinary temperature. The oxychlorides obtained are only stable in the neutral salt solution, and are decomposed by water into mercuric chloride and oxide. They are not decomposed to any extent by alcohol. The formation of basic salts is not due to the slight solubility of the calcium carbonate in water, for when three sealed tubes containing marble, mercuric chloride and water, alcohol, and ether respectively were heated at 96° for 120 hours, and then at 110—125° for three hours, oxychlorides were formed only in that tube containing water. Oxychlorides were also obtained by heating mercuric chloride with water only at 210° for 48 hours.

E. C. R.

**Cerite Earths.** By PAUL SCHÜTZENBERGER (*Compt. rend.*, 1895, 120, 962—966).—The first and most abundant crystallisations of cerium sulphate (this vol., ii, 352), when subjected to repeated fractional crystallisation, yield a product of constant composition, which gives the following results for the atomic weight of cerium:—By conversion into dioxide at a cherry-red heat,  $\text{Ce}_1 = 139.5$ ; by analysis with barium chloride (*loc. cit.*),  $\text{Ce}_1 = 139.5$ ; conversion into dioxide at a bright red heat,  $\text{Ce}_1 = 129.0$  to 138.8. The synthesis of the sulphate from the dioxide obtained by heating the oxalate in air yields results which vary with the temperature at which the oxalate has been heated; at a dull redness,  $\text{Ce}_1 = 142$  to 143; at a cherry-red heat,  $\text{Ce}_1 = 139.7$ ; at a bright red heat,  $\text{Ce}_1 = 139.0$  to 138.8.

The sulphate precipitated by alcohol from the last mother liquors and purified by recrystallisation yields different results, and may be distinguished as  $\text{Ce}_2$ . It is free from yttrium, didymium, and lanthanum, and forms with potassium sulphate a double salt quite insoluble in a saturated solution of potassium sulphate. When precipitated with barium chloride,  $\text{Ce}_2 = 138.75$ , whereas the various

synthetical methods give  $Ce_2 = 135.7$  to  $142.5$  according to the temperature at which the oxide was heated. It is noteworthy that the values obtained for  $Ce_1$  by precipitation of the sulphuric acid with barium chloride and by heating the sulphate at a cherry-red heat are practically identical, whereas, in the case of  $Ce_2$  there is a considerable difference; it would seem that the oxide of  $Ce_2$  is more readily decomposed on heating.

The final mother liquors obtained in the preparation of the cerium sulphate yield a product which may be distinguished as  $Ce_3$ . Precipitation with barium chloride gives  $Ce^3 = 137.1$ , whilst the synthetic method gives  $Ce^3 = 142.4$ , and the action of heat on the sulphate  $Ce = 128$  to  $130$ .

It follows from these results that in cerite, cerium is accompanied by small quantities of another metal of lower atomic weight which forms a sulphate isomorphous with cerium sulphate, and a dioxide which has a distinctly reddish colour, and seems to be more readily decomposed by heat than cerium dioxide. C. H. B.

**Amalgamated Aluminium as a Reducing Agent.** By JULIUS B. COHEN and REGINALD ORMANDY (*Ber.*, 1895, **28**, 1505—1506).—The authors point out that the reducing properties of amalgamated aluminium, which form the subject of a recent paper by Wislicenus and Kaufmann (this vol., i, 437), were described by them in 1889 (*Brit. Assoc. Rep.*, 1889, 550), and that the application of this reducing agent to water analysis formed the subject of a paper published in the Journal of the Chemical Society (*Trans.*, 1890, 811). They are at present engaged in the further study of the properties of the amalgam as a reducing agent. A. H.

**Manganese Compounds.** By CHARLES LEPIERRE (*Compt. rend.*, 1895, **120**, 924—926).—The compound  $(NH_4)_2SO_4 \cdot 2MnSO_4$  is obtained by adding crystallised manganous sulphate to about five times its weight of fused ammonium sulphate. The fused salt is decanted off from the crystals, and the latter are purified by treatment with boiling alcohol of  $70^\circ$ . They are white or pale yellow, anhydrous, and somewhat bulky, and belong to the cubic system; sp. gr. =  $2.56$  at  $14^\circ$ , which is practically the mean sp. gr. of the constituents. The double salt is readily decomposed by water.

Anhydrous manganous sulphate is obtained crystallised by heating the preceding salt at  $350^\circ$  alone or in presence of the mother liquor, the excess of ammonium salt being expelled below a dull red heat. The crystals are very hygroscopic; sp. gr. =  $3.14$  at  $12^\circ$ .

It will be observed that manganese behaves like nickel and cobalt (*Abstr.*, 1892, 1282), and does not, like iron (*Abstr.*, 1892, 943), yield more highly oxidised compounds.

The salt  $(NH_4)_2SO_4 \cdot Mn_2(SO_4)_3$ , or anhydrous manganese alum, is formed on adding a mixture of equal volumes of nitric and sulphuric acids to the preceding double salt in presence of excess of the ammonium compound, and separates in violet-brown, hexagonal crystals, which can be purified by treatment with hot concentrated sulphuric acid, glacial acetic acid, and, finally, dry ether. The crystals (sp. gr.

$= 2.40$  at  $11^{\circ}$ ) are decomposed by water with formation of pseudo-morphic manganic oxide; they are insoluble in ether, benzene, and concentrated sulphuric acid, but dissolve in a mixture of equal volumes of sulphuric acid and water. When heated alone or in the liquid in which it was formed, the double salt decomposes with evolution of sulphuric anhydride and oxygen, and formation of the manganous ammonium sulphate.

By adding ferric, chromic, or aluminium sulphates, or potassium, sodium, and, perhaps, thallium sulphates, mixed anhydrous manganese alums can be obtained similar to those described by Klobb (*Abstr.*, 1893, ii, 572).

When hydrated manganous sulphate is fused with 10 times its weight of potassium nitrate for several hours, the oxide  $\text{MnO}, 5\text{MnO}_2$  is obtained in crystals of sp. gr. 3.41. Under similar conditions, manganous carbonate yields the oxide  $\text{Mn}_2\text{O}_3$ , in a confusedly crystalline form, and manganous nitrate yields the oxide  $\text{MnO}, 3\text{MnO}_2$ .

C. H. B.

**Action of Ferric Chloride on Metallic Iodides.** By KARL SEUBURT and KARL GAAB (*Zeit. anorg. Chem.*, 1895, 9, 212—227).—The quantity of iodine liberated by the action of ferric chloride on the different iodides is approximately equal, and the curves illustrating the action are very similar. Disregarding small anomalies, the following iodides are arranged according to the ease with which they are decomposed—ferric iodide, cadmium iodide, zinc iodide, potassium iodide, lithium iodide, magnesium iodide, calcium iodide, sodium iodide, strontium iodide, barium iodide, manganese iodide, ammonium iodide, aluminium iodide. Aluminium iodide shows a great anomaly; it gives a 5 per cent. higher decomposition than the other iodides and is the only iodide, except hydrogen iodide, which when employed in excess with ferric chloride liberates the theoretical quantity of free iodine. This point is reached in the case of hydrogen iodide at 15 equivalents, in the case of aluminium iodide at seven equivalents for one equivalent of ferric chloride. Considerably lower quantities of iodine are obtained with cadmium and ferric iodide when these are employed in excess. In the case of lithium iodide, the amount of iodine liberated increases until 5 mols. of iodide to one equivalent of ferric chloride are present, and then decreases again; at the same time basic salts are precipitated.

The final results obtained with an excess of iodide, and with an excess of ferric salt are very similar, the curves obtained, however, rise more gradually with an excess of ferric salt than of iodide as has already been shown for potassium iodide, and hydrogen iodide (*Zeit. anorg. Chem.*, 5, 419). The decomposition with an excess of ferric salt gives the theoretical quantity of free iodine when 16 equivalents are present, whereas only 96.8 per cent. of the theoretical quantity of free iodine is obtained with 18 equivalents of iodide.

The influence of the base which is present in the iodide is, as a rule, very small, and very much less than the influence of the acid radicle in the ferric salt, which has already been shown in the case of ferric sulphate and acetate.

E. C. R.

**Volatility of Chromic Anhydride.** By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1895, 9, 29—30).—Chromic anhydride can be melted without decomposition, but on raising the temperature there is a violent evolution of oxygen together with red vapours which are apparently chromic anhydride. When perfectly dry chromic anhydride is heated in a vacuum for 20 hours at 110—130°, a small quantity is volatilised, and after heating at 125° for four days long, red needles of chromic anhydride were obtained. E. C. R.

**Tungsten and Molybdenum and their Trioxides.** By CHARLES H. EHRENFELD (*J. Amer. Chem. Soc.*, 1895, 17, 381—397).—Tungsten trioxide, when heated with an equivalent weight of phosphoric chloride in an atmosphere of carbonic anhydride is converted into the hexa- and penta-chlorides, and phosphorous oxychloride is evolved. The product is red-brown, melts to a dark red liquid, and gives off reddish-brown vapours resembling bromine; these condense to steel-blue isometric forms of the hexachloride mixed with reddish-brown needles of the pentachloride. The intensity of the heat applied, and the duration of the action determine the quantity of the brown material produced. This is not surprising, since the hexachloride passes into the pentachloride by ignition in carbonic anhydride or hydrogen. The analysis of another, bright red, and more volatile product, showed it to be tungsten oxytetrachloride,  $\text{WOCl}_4$ . The same reaction takes place in an atmosphere of nitrogen, but less satisfactorily.

With a mixture of equivalent quantities of molybdenum trioxide and phosphoric chloride, the action takes place at a lower temperature, and is more rapid and energetic: molybdenum pentachloride is produced, mixed with small quantities of lower chlorides.

No action takes place when tungsten trioxide is heated with silicon tetrachloride in an atmosphere of carbonic anhydride. When a small quantity of air is introduced, tungsten oxytetrachloride and tungstyl chloride are formed. Silicon tetrachloride is likewise without action on molybdenum trioxide.

*Action of various Gases on Tungsten and Molybdenum.*—Tungsten and molybdenum trioxides remain unchanged when heated in a current of nitric oxide. When finely powdered tungsten is heated in a current of nitric oxide, the action commences below a red heat, and the substance becomes white hot. The product is tungsten trioxide. With molybdenum, the action is less energetic and molybdenum dioxide is produced. When heated with nitrous oxide, tungsten is converted into the trioxide, but the action is less energetic than with nitric oxide. Molybdenum when treated in the same manner, required a full red heat before any action took place, the product being molybdenum dioxide. With nitrogen peroxide and tungsten, action commences at about 300—350°, and then proceeds rapidly, the trioxide being formed. With molybdenum, the action begins at an incipient red heat, proceeds with more energy than in the preceding instances, and at once forms molybdenum trioxide. With sulphurous anhydride, tungsten is slowly oxidised at a moderately high temperature, lower tungsten oxides being formed and sulphur deposited. With molybdc-

num, the action takes place only at the highest temperature and molybdenum dioxide is formed. No action takes place when tungsten or molybdenum is heated in a current of methylamine.

*Action of various Gases on Tungsten and Molybdenum Trioxides.*—Tungsten trioxide, when heated in a current of ethylene, is slowly reduced at a red heat and water and carbon are formed; the product is a deep blue oxide which does not precipitate metallic silver from an ammoniacal solution. Molybdenum trioxide when treated in a similar manner yields a beautiful, bronze coloured, crystalline oxide which dissolves in an ammoniacal silver solution with deposition of metallic silver, and on analysis gave numbers agreeing with the formula,  $\text{Mo}_2\text{O}_5$ . When heated in a current of acetylene, tungsten trioxide is slowly reduced to a mixture of brown and blue oxides. Molybdenum trioxide is reduced much more readily, and the same bronze-brown oxide is obtained as with ethylene; underlying this oxide there is a shining, crystalline, metallic product, which the author believes to be a molybdenum carbide of the formula  $\text{Mo}_2\text{C}$ , or  $\text{Mo}_3\text{C}$ . Tungsten trioxide is not reduced by methane at the highest heat of a Bunsen burner, but at the full heat of a blast-lamp, the trioxide is reduced to the blue oxide,  $\text{W}_2\text{O}_5$ . Molybdenum trioxide is reduced at the ordinary heat of a Bunsen flame, the dioxide being formed; neither of the trioxides is affected by ethane. Tungsten trioxide, when heated with phosphine is reduced at about  $125-150^\circ$ ; the product is a deep-blue oxide of the composition  $\text{W}_3\text{O}_8$ , and contains about 2 per cent. of phosphorus mechanically mixed with it. Molybdenum trioxides begin to show signs of reduction without the application of heat, and when gently heated the action proceeds rapidly; a beautiful lustrous purple oxide is formed which, on analysis, gives numbers agreeing with the formula,  $\text{Mo}_2\text{O}_5$ ; it contains about 2 per cent. of phosphorus. Ammonia acts on tungsten and molybdenum trioxides more energetically, and the products are very complicated. With arsenic, the products are the same as with phosphine, but the reduction takes place much more sluggishly. As usual, molybdenum trioxide is the more readily reduced.

*Reduction of the Trioxides by Magnesium, Zinc, and Aluminium.*—Tungsten trioxide when heated with powdered magnesium is reduced to the dioxide; when the reaction takes place in an atmosphere of hydrogen, light is emitted and heat produced sufficient to crack the combustion tube. On analysis, the dark-gray product gave numbers agreeing with those required for the sesquioxide. Molybdenum trioxide, when treated in a similar way yields the sesquioxide if reduced in air, and the dioxide if reduced in hydrogen. With zinc and tungsten trioxide, the reduction takes place at about  $300-400^\circ$ , and in air a lower oxide,  $\text{W}_2\text{O}_5$ , is formed; in hydrogen the dioxide is formed. Molybdenum trioxide is reduced more readily, and in air the product is probably  $\text{Mo}_2\text{O}_5$ ; in hydrogen, a brown mixture is formed which, on analysis, gave numbers agreeing with the composition  $\text{Mo}_2\text{O}_5$ . When tungsten trioxide is heated with aluminium in a tube sealed at one end, no action took place until a full red heat is reached, when there is a flash and slight report, cracking the tube and scattering its contents. With molybdenum trioxide, the action



is similar, and the blue oxide,  $\text{Mo}_2\text{O}_5$ , is formed. When heated in hydrogen with aluminium, no action takes place, probably for the reason that the temperature required is so high that the trioxides are reduced by the hydrogen before the aluminium can act.

The above experiments show that there is a considerably stronger affinity between tungsten and oxygen than there is between molybdenum and oxygen.

*Reduction of Ferric Chloride by Tungsten and Molybdenum.*—Molybdenum reduces a solution of ferric chloride according to the equation,  $6\text{FeCl}_3 + \text{Mo} = \text{MoCl}_6 + 6\text{FeCl}_2$ . Complete reduction does not, however, take place in a reasonable length of time, except with small quantities of the metal; thus using 0.67857 gram molybdenum, only 97.10 per cent. of the molybdenum had gone into solution after 48 hours. With tungsten, a similar reduction takes place but the action is extremely slow; there is a gradual increase in the amount of iron reduced, roughly proportional to the time, but complete solution of the tungsten cannot be obtained.

E. C. R.

**New Source of Uranium.** By NORDENSKIÖLD (*Compt. rend.*, 1895, 120, 859).—The author has discovered a bed of carbonaceous sedimentary rock, the ashes of which contain from 2 to 3 per cent. of uranium. It also contains a small quantity of nickel and rare earths, and a considerable quantity of nitrogen, and the author suggests that it may possibly be an abundant source of argon or helium.

C. H. B.

**Double Halogen Salts of Caesium, Rubidium, Sodium, and Lithium with Thallium.** By J. H. PRATT (*Zeit. anorg. Chem.*, 1895, 9, 19—28).—The salts described in this paper belong to four types, caesium giving a more complete series than the other alkali metals. The ease of formation and the number of salts increases from the iodides to the chlorides. The salts with alkali metals of lower atomic weight are generally more easily soluble in water, form larger crystals, and contain more water of crystallisation.

3:1-Caesium and rubidium thallium chlorides,  $\text{Cs}_3\text{TlCl}_6 + \text{H}_2\text{O}$ , and  $\text{Rb}_3\text{TlCl}_6 + \text{H}_2\text{O}$ .—The caesium salt is obtained as a white precipitate when 0.25 gram of thallium chloride is added to a solution of 50 grams of caesium chloride; it dissolves on gently warming the solution, and crystallises in very slender needles. The conditions of formation are very narrow, as if 3 grams of thallium chloride are employed, the salt,  $\text{Cs}_2\text{TlCl}_6$ , is formed. The rubidium salt is formed when 1.5—25 grams of thallium chloride is added to a solution of 40 grams of rubidium chloride. It crystallises in thin monoclinic plates, and when recrystallised from water is converted into the salt  $\text{Rb}_2\text{TlCl}_5 + \text{H}_2\text{O}$ .

2:1-Caesium and rubidium thallium chlorides,  $\text{Cs}_2\text{TlCl}_5$ ,  $\text{Cs}_2\text{TlCl}_5 + \text{H}_2\text{O}$ , and  $\text{Rb}_2\text{TlCl}_5 + \text{H}_2\text{O}$ .—The anhydrous caesium salt is obtained when 5—8 grams of thallium chloride is added to a somewhat concentrated solution of 100 grams of caesium chloride, the hydrated salt being obtained when dilute solutions are employed. The rubidium salt is obtained in a similar manner. The hydrated

salts are white, the anhydrous salts pale green. The caesium salt, with  $1\text{H}_2\text{O}$ , is easily soluble in water, but separates out anhydrous in the form of needles. The salt,  $\text{Cs}_2\text{TlCl}_6 + \text{H}_2\text{O}$ , crystallises in the orthorhombic system  $a : b : c = 0.6762 : 1 : 0.6954$ . The crystals of the rubidium salt are also orthorhombic,  $a : b : c = 0.6792 : 1 : 0.7002$ .

3:2-Caesium thallium chloride,  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ , is obtained as a heavy white precipitate on adding 5—29 grams of caesium chloride to a solution of 40 grams of thallium chloride. It crystallises in hexagonal prisms or tablets, axis  $C = 0.82566, 0001 \wedge 10\bar{1}1 = 43^\circ 37' 50''$ . The salt is stable on exposure to air, and can be recrystallised from water without change.

3:1-Rubidium thallium bromide,  $\text{Rb}_3\text{TlBr}_6, \text{H}_2\text{O}$ , is obtained by adding 1.5—24 grams thallium bromide to a very concentrated solution of 50 grams of rubidium bromide. It crystallises in beautiful golden crystals belonging to the tetragonal system: axis  $C = 0.80725; 001 \wedge 101 = 38^\circ 54' 45''$ . When recrystallised, it is converted into the 1:1-salt. The author was unable to obtain a 2:1- or a 3:2-rubidium salt.

3:2-Caesium thallium bromide,  $\text{Cs}_3\text{Tl}_2\text{Br}_9$ , crystallises in small, yellowish-red crystals, is stable in air, and can be recrystallised unchanged from water.

1:1-Caesium and rubidium thallium bromides,  $\text{CsTlBr}_4$ , and  $\text{RbTlBr}_4 + \text{H}_2\text{O}$ .—The caesium salt is obtained by adding 2—10 grams of caesium bromide to 40 grams of thallium bromide, and the rubidium salt, by adding 3—24 grams of rubidium bromide to 40 grams of thallium bromide. Both salts are pale yellow, and crystallise in the regular system. The rubidium salt crystallises from water unchanged, whereas the caesium salt is converted into the salt,  $\text{Cs}_3\text{Tl}_2\text{Br}_9$ .

1:1-Caesium and rubidium thallium iodides,  $\text{CsTlI}_4$  and  $\text{RbTlI}_4 + 2\text{H}_2\text{O}$ .—Both salts are obtained from solutions containing a large excess of thallium iodide, and also of alkali iodide; they form deep-red crystals, belonging to the regular system, have a characteristic lustre which is slowly lost on exposure to air, and are decomposed by water.

3:1-Sodium and lithium thallium chlorides,  $\text{Na}_3\text{TlCl}_6 + 12\text{H}_2\text{O}$  and  $\text{Li}_3\text{TlCl}_6 + 8\text{H}_2\text{O}$ .—The author was only able to obtain one type of double salt with these metals, and, on account of the extreme solubility of the salts, they must be prepared in very concentrated solutions. They form transparent colourless crystals which break up on exposure to air. The author was unable to prepare lithium or sodium thallium bromide.

E. C. R.

**Phenomena observed in the Precipitation of Antimony from Solutions of Tartar Emetic.** By J. H. LONG (*J. Amer. Chem. Soc.*, 1895, ii, 87—105).—A study in chemical dynamics. The action of sodium carbonate, sodium borate, sodium tungstate, and sodium thiosulphate on solutions of tartar emetic is described. The experiments were conducted with the object of studying the influence of mass, temperature, and time on the precipitation of the antimony.

L. DE K.

**Constitution of the Platinum Bases.** By PETER KLASON (*Ber.* 1895, 28, 1477—1489).—The author enters into an elaborate critical account of the various theories of the constitution of the platinum ammonium compounds, and shows that the constitution of the compounds hitherto known can be expressed by the aid of structural formulæ, without having recourse to geometrical isomerism, and in fact that the geometrical theory of Werner is in part founded on imperfectly investigated reactions (see also this vol., i, 488).

A. H.

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## Mineralogical Chemistry.

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**Italian Graphites.** By FAUSTO SESTINI (*Gazzetta*, 1895, 25, i, 216—219).—With the object of ascertaining whether the natural carbons found in various parts of Italy are all graphitites, like the two specimens recently described, the author has examined a number of samples from Monte Pisano, Arbure, Monte Rosa, Calabria, Premolle, and Monte Amiati. Three of these are true graphites, containing not more than 0·87 per cent. of hygroscopic water, and not less than 57·1 per cent. of carbonaceous matter; the several graphitites examined, however, contain more than 1 per cent. of water, not more than 51·36 per cent. of carbonaceous matter, and 43·33—84·42 per cent. of mineral matter not easily decomposed by hydrofluoric acid.

W. J. P.

**Genetic Relations of Rutile, Ilmenite, and Sphene.** By ALFRED BERGEAT (*Jahrb. f. Min.*, 1895, i, 232—251).—It is usually supposed that sphene (including leucosene and titanomorphite) which occurs intergrown with, and surrounding, rutile and ilmenite, has been derived from the alteration of these minerals, the ilmenite being also derived from the rutile. The author, however, describes at length occurrences of these minerals near Freiberg, which point to their all being original, having crystallised from a magma in the order, rutile, ilmenite, sphene, as is seen by the envelopes of the later formed minerals surrounding the earlier. The intergrowth of rutile and ilmenite is considered to be analogous to that of rutile and hæmatite, and several similar cases of regular intergrowth of dissimilar minerals are noticed. Analyses are given of some of these envelopes surrounding rutile: I is a greyish, opaque substance, showing under the microscope some crystals of sphene; II is a still more advanced stage in the decomposition of sphene, and shows crystals of anatase.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Total.
I.	45·56	46·01	3·83	2·72	99·12
II.	14·27	78·13	7·24	0·88	100·52

These analyses show that as sphene decomposes there is a gradual decrease in the amount of silica and lime, and an increase in titanium

oxide, which separates as anatase (in I, free quartz was present; the iron oxide is supposed to be foreign, and due to infiltration).

L. J. S.

**Artificial Dolomite.** By LÉON BOURGEOIS and HERMANN TRAUBE (*Zeit. Kryst. Min.*, 1895, **24**, 519; from *Bull. soc. fran. min.*, 1892, **15**, 13).—On heating a solution of potassium cyanate containing equivalent proportions of calcium and magnesium chlorides at 130°, needles of aragonite and rhombohedral crystals were obtained, the latter having the composition, CaO 28·49, MgO 24·24.

L. J. S.

**Microkite, Parisite, and Elpidite from Greenland.** By GUSTAF NORDENSKJÖLD (*Jahrb. f. Min.*, 1895, i, Ref., 455—457; from *Geol. För. Förh.*, 1894, **16**, 336).—*Microkite* was found as minute, brownish-yellow octahedra on ægirine from Igaliko.

(Ta,Nb) <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	SnO <sub>2</sub> .	(Fe,Al) <sub>2</sub> O <sub>3</sub> , (Ce,La,Di) <sub>2</sub> O <sub>3</sub> .	CaO.	Loss.
54·8	13·5	3·0	12·2	9·6	6·9

After deducting the constituents required for the amount of ægirine, corresponding to 13·5 per cent. of silica, the formula is deduced as essentially Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>; very little niobium is present.

*Parisite*, in yellow crystals, generally consisting of the basal plane, with two acute rhombohedra of different orders, was also found on ægirine from the same locality. Analysis gave the following results.

CO <sub>2</sub> .	(Ce,La,Di) <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss.
23·0	52·1	2·2	0·7	2·5	12·2	0·7	1·5	5·1

*Elpidite* (see below).—The small crystals are orthorhombic and elongated in the direction of the vertical axis; the observed forms are *a*(100), *b*(010), *c*(001), *m*(110), *n*(120), *d*(011), *e*(103); *a*:*b*:*c* = 0·5117:1:0·9781.

There are also observations on Flink's new minerals, epididymite, and neptunite from the same locality.

L. J. S.

**Analysis of Fyreneite.** By EDUARD JANNETTAZ (*Zeit. Kryst. Min.*, 1895, **24**, 522; from *Bull. soc. fran. min.*, 1892, **15**, 127).—Crystals from Barèges gave the following results, after deducting water and carbonic anhydride.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Total.
39·4	10·0	18·6	1·0	31·2	100·2

This indicates an excess of silica, perhaps as enclosed quartz. Sp. gr. 3·7.

L. J. S.

**Elpidite, a New Mineral from Greenland.** By GUSTAF LINDSTRÖM (*Jahrb. f. Min.*, 1895, i, Ref., 457; from *Geol. För. Förh.*, 1894, **16**, 330).—*Elpidite* was found, together with Flink's new minerals, epididymite and neptunite (this vol., ii, 23 and 402), on ægirine from Igaliko; it is white to brick-red in colour, and fibrous, with a silky lustre. Sp. gr. varies from 2·524 to 2·594, according to the colour; easily fusible. Analysis of the mineral gave the following results.

SiO <sub>2</sub> .	ZrO <sub>2</sub> .	FeO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O (at 100° C.).
59·44	20·48	0·14	0·17	10·41	0·13	3·89
H <sub>2</sub> O (above 100° C.).	Cl.	TiO <sub>2</sub> .	CuO.	Total.		
5·72	0·15	trace	trace	100·53		

The ratio is given as  $\text{ZrO}_2 : (\text{FeCaNa}_2\text{K}_2)\text{O} : \text{H}_2\text{O} : \text{SiO}_2 = 1 : 1 : 3 : 6$ , it being impossible to say what parts the zirconia and water play in the formula.  
L. J. S.

**Neptunite.** By O. A. SJÖSTRÖM (*Jahrb. f. Min.*, 1895, i, Ref., 457; from *Geol. För. Förh.*, 1893, 15, 393).—This new mineral of Flink's (this vol., ii, 23) gave the following results on analysis.

SiO <sub>2</sub> .	TiO <sub>2</sub> .	FeO.	MnO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
51·93	17·45	10·23	5·32	0·71	5·71	9·63	100·98
							L. J. S.

**Meteoric Iron of Verchne-Udinsk (Werchne Udinsk), Siberia.** By E. A. HUGO LASPEYRES and E. KAISER (*Zeit. Kryst. Min.*, 1895, 24, 493—494).—A piece of this meteorite weighing 2·3547 grams was slowly dissolved in cold dilute hydrochloric acid; the gases evolved indicated that only a trace of triolite was present. The insoluble residue consisted of a scaly, graphite-like substance, silicate grains (probably quartz and enstatite), and schreibersite and rhabdite; the solution contained iron, nickel, cobalt, copper, magnesium, and phosphorus. The phosphorus in the solution is calculated as iron nickel phosphide, and the composition of the meteorite is as follows.

Nickel-iron.	Fe-Ni phosphide.	Graphite.	FeS.	Silicates.
98·812	0·565	0·025	trace	0·008 = 99·410

The nickel-iron gave the following results on analysis.

Fe.	Ni.	Co.	Cu.	Mg.
91·782	7·346	0·709	0·129	0·034

The ratio  $\text{Fe} : \text{Ni} + \text{Co} = 1 : 12$  agrees with that for kamacite. The very small amount of ténite, seen to be present by the etching, was dissolved by the cold dilute acid.  
L. J. S.

**Silicates of the Netschaëvo (Tula) Meteorite.** By E. A. HUGO LASPEYRES and E. KAISER (*Zeit. Kryst. Min.*, 1895, 24, 495—496).—The angular fragments and nests of stony matter of this iron were treated with hot hydrochloric acid; much hydrogen sulphide was evolved, and the solution contained iron, magnesium, trace of aluminium, some calcium and nickel, these corresponding with the original constituents, triolite and olivine, and a little nickel-iron and plagioclase. The gelatinous residue was seen under the microscope to consist of enstatite and, perhaps, some quartz and plagioclase. The solution of this residue in hydrofluoric acid contained much magnesium, little iron, aluminium, and calcium, and a trace of sodium; these corresponding with enstatite and, perhaps, some plagioclase.

L. J. S.

## Physiological Chemistry.

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**Action of Thiocyanic acid on Gastric Ferments.** By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1895, **28**, 1719—1722).—Thiocyanic acid is without action on pepsin solutions, but, even in the proportion 1 : 50 of hydrochloric acid, it retards considerably the digestion of carmin-fibrin by pepsin. Potassium thiocyanate and ammonium thiocyanate behave like the free acid. The coagulation of milk by means of rennin is considerably retarded by the presence of potassium thiocyanate; neither result is due to any specific action on the ferment, but in the former case the thiocyanate coagulates the carmin-fibrin and so withdraws it to a great extent from the action of the pepsin; in the latter, a double decomposition probably occurs, and the casein dissolves. The experiments are fully tabulated. J. B. T.

**Action of the Mucous Membrane of the Stomach and Intestine on some Bioses and on Raffinose.** By WALTHER PAUTZ and J. VOGEL (*Zeit. Biol.*, 1895, **32**, 304—307).—The hydrolytic action of the mucous membrane of the small intestine on maltose has been shown by several previous observers. In the present experiments, the gastric mucous membrane of dogs and new-born children was employed, as well as the intestinal, the sugars investigated being isomaltose, lactose, and raffinose. At the end of 18, and again at the end of 36 hours, the sugar was investigated by the polarimeter, phenylhydrazine test, &c. The stomach, ileum, and large intestine only effected a partial inversion of maltose and isomaltose, but the jejunum had turned them completely into dextrose. The stomach, ileum, and large intestine had no effect on lactose; but the jejunum effected a partial change into dextrose. In the last case, besides dextrosazone, an osazone melting at 142° was also obtained.

W. D. H.

**Comparison of the Ferment Actions of Saliva, Pancreatic Juice, Intestinal Juice, and Blood on Starch.** By CARL HAMBURGER (*Pflüger's Archiv.*, 1895, **60**, 543—577).—A comparison of the action of the above-mentioned liquids on starch shows differences in two directions. The maximum of reducing action shown in the same time (24 hours) is different, and this maximum is reached more rapidly in some cases than others. The maximum of reduction for saliva is 0.31; for pancreatic juice, 0.36; for intestinal juice, 0.26; and for blood, 0.8, the reducing power of dextrose being taken as 1. In the case of saliva, this is reached within an hour, in that of blood after 24 hours; pancreatic juice is quicker than saliva, and intestinal juice slower than blood. Saliva thus acts rapidly, but the reducing value of the product is low; blood acts slowly, but the reducing value of the product is very high, the difference of reducing value depending on the different forms of sugar produced. With saliva, the sugar yields, on suitable treatment, after the dextrins have disappeared,

maltosazone and isomaltosazone, but very little glucosazone. In the case of blood, much glucosazone is obtained (compare Bial). Probably two ferments are to be reckoned with, diastase, which transforms starch into dextrins and maltose, and glucase, which transforms it into glucose, perhaps through a maltose stage. The latter ferment is specially abundant in blood; saliva contains more diastase than blood or intestinal juice. Pancreatic juice is even richer in this ferment. But glucase is nearly absent in saliva, though fairly abundant in pancreatic juice. Intestinal juice, on the other hand, contains still less diastase than blood, more glucase than saliva, but less than the blood and pancreatic juice. W. D. H.

**Digestibility of Pentosans.** By LINDSEY and HOLLAND (*Bied. Centr.*, 1895, **24**, 311—312; from *Agric. Science*, 1894, **8**, 172—183).—Pentosans which yield xylose occur frequently in agricultural plants, whilst those which yield arabinose are found in the sap of many plants. In experiments with rabbits fed with maize-meal and bran, Stone found about 60 per cent. of the pentosans were digested; similar results were obtained with sheep fed with hay.

Experiments made with hay, brewers' grains, linseed meal, wheat bran, &c., showed that in six cases out of nine, the pentosans were just as digestible as the other food constituents. In foods such as hay and grains in which lignin predominates, the pentosans are less digestible than in the concentrated foods.

The question still remains whether the pentosans are assimilated and have a real value. N. H. J. M.

**Relation of Fat and Carbohydrates to the Decomposition of Albumin in the Human Body.** By R. KAYSER (*Bied. Centr.*, 1895, **24**, 344; from *Diss. Berlin*, 1893).—Experiments made by the author on himself, showed that fat was much less able to maintain the albumin equilibrium in the body than isodynamic amounts of carbohydrates.

To maintain nitrogen equilibrium with proteids and fat alone, a very great amount of potential energy is necessary, far in excess of the total requirements; whilst deposition of albumin seems to be excluded under these conditions.

The experiments lasted only a very short time, and it is not known, therefore, whether the conclusions would hold for longer periods. In the meantime, the advisability of employing a pure meat fat diet for diabetes must be considered questionable. N. H. J. M.

**Does Inulin lead to the Formation of Glycogen in Vegetable Feeders?** By K. MIURA (*Zeit. Biol.*, 1895, **32**, 255—265).—The experiments made on rabbits show that after six days inanition, the taking of inulin often leads to the formation of small quantities of hepatic glycogen, especially when the dose is large. Levulose is found in the intestine in most cases. The change into levulose is slow and not complete; the inconstancy of the result on the hepatic glycogen is probably due to this circumstance. W. D. H.



**The Inversion of Cane Sugar in the Small Intestine.** By K. MIURA (*Zeit. Biol.*, 1895, 32, 266—278).—The invertin of the small intestine does not depend on the introduction of food, for it is found in those born dead. It is also independent of bacterial action, for the intestine of those just born is free from micro-organisms. Stomach, colon, and pancreas have an exceedingly weak inverting action.  
W. D. H.

**Exchange of Blood-gases in Brain and Muscle.** By LEONARD HILL and D. N. NABARRO (*J. Physiol.*, 1895, 18, 218—229).—A full account of experiments, a preliminary notice of which has already appeared (this vol., ii, 231). The small increase of gas exchange in the brain during activity entirely negatives Mosso's statement that the brain is a tissue where only active metabolism occurs.  
W. D. H.

**Grape Sugar in Blood.** By K. MIURA (*Zeit. Biol.*, 1895, 32, 279—280).—In ox blood, the sugar present is dextrose, identified by its osazone.  
W. D. H.

**Physiological Action of Extract of Suprarenal Capsule.** By EDWARD A. SCHÄFER and GEORGE OLIVER (*J. Physiol.*, 1895, 18, 230—276).—A full account with numerous illustrative tracings of experiments already described in a preliminary notice (this vol., ii, 235).  
W. D. H.

**Physiological Action of Extracts of Pituitary Body.** By EDWARD A. SCHÄFER and GEORGE OLIVER (*J. Physiol.*, 1895, 18, 277—279).—Extract of pituitary body raises, of thyroid lowers, of spleen first lowers, then raises, the blood pressure. In the first case, the very marked rise is due to increase of the heart's force, and contraction of the arterioles. The opposite action of thyroid and pituitary extracts negatives the idea that the two glands are vicarious in function.  
W. D. H.

**Heat Production in Glands.** By E. WAYMOUTH REID (*Proc. physiol. Soc.*, 1895, 31—33).—The production of heat in secreting glands when stimulated to activity by excitation of nerves cannot be demonstrated by any apparatus at present devised for detecting small changes in temperature. (Compare Bayliss and Hill, *Abstr.*, 1894, ii, 358.)  
W. D. H.

**Gases of Human Milk.** By EDUARD KÜLZ (*Zeit. Biol.*, 1895, 32, 180—184).—In five researches, 100 c.c. of human milk yielded 1.07 to 1.44 c.c. of oxygen, 2.35 to 2.87 c.c. of carbonic anhydride, and 3.37 to 3.81 c.c. of nitrogen. The method of collecting the milk could not have obviated admixture with minimal quantities of air; hence, perhaps, the higher percentage of oxygen and nitrogen than previous observers have found in the milk of lower animals.  
W. D. H.

**Paralactic acid in Normal Pericardial Fluid.** By C. KÜLZ (*Zeit. Biol.*, 1895, 32, 252—254).—The normal pericardial fluid of

the ox contains paralactic acid, identified by polarimetric observation and by analysis of its zinc salt.

W. D. H.

**Metabolism in Diabetes.** By WALTHER PAUTZ (*Zeit. Biol.*, 1895, **32**, 197—251).—The research was carried out by analysing the food taken, and the excreta, urine, and fæces. As many as 24 diabetic patients were investigated; the results in each case are given in full. In none of these cases was there any increase of metabolism, so far as proteid and fat are concerned; indeed, in 11 cases it was lessened, but the differences are small, and differences as great are found in healthy people, similar observations on four of whom served as control experiments.

W. D. H.

**Alimentary Glycosuria.** By K. MIURA (*Zeit. Biol.*, 1895, **32**, 281—303).—Experiments were made on a boy, a man, and dogs, by administering large amounts of different kinds of carbohydrate, and examining the urine by the polarimeter, and by Fehling's, the fermentation, and the phenylhydrazine tests. Starch, even in very large doses, does not lead to glycosuria. Dextrose does pass into the urine; thus, after a dose of 345 grams, 0.7 gram was found in the urine. Lævulose is not borne well, causing sickness and diarrhœa in large doses; from 0.6 to 2.7 per cent. passed as such into the urine. Maltose in man caused no glycosuria; in dogs, 2.8 per cent. passed into the urine as such; but when given as beer-wort, a small quantity of dextrose was found. 1.08 per cent. of cane sugar passed as such into the urine, but in dogs a larger quantity was found together with invert sugar. In both dogs and men, milk sugar passed as such into the urine, to the extent of 2 to 4 per cent. In some cases, several of the sugars were found in small quantities in the saliva as well as the urine.

W. D. H.

**Pentoses in Diabetic Urine.** By EDUARD KÜLZ and J. VOGEL (*Zeit. Biol.*, 1895, **32**, 185—196).—Tollen's reaction for pentoses failed in 64 specimens of human diabetic urine, was doubtful in 12, and positive in 4 only. But in diabetes of the severe form produced in dogs by extirpation of the pancreas, or administration of phloridzin, the reaction is given well. Pentose was identified by its osazone, which was separated from glucosazone by its solubilities, but the pentose differs from those hitherto described in being fermentable with yeast. Its osazone melts at 150—158°, the melting point varying slightly in the different cases, which are described in full; analyses of the osazone agrees very well with the formula  $C_{17}H_{20}N_4O_8$ .

W. D. H.

**Apparent Presence of Sugar in the Urine of Persons taking Sulphonal.** By PH. LAFON (*Compt. rend.*, 1895, **120**, 933).—The urine of a person who was taking 0.75 to 1.0 gram of sulphonal per day gave a distinct reduction with Fehling's solution, although, instead of the dextrorotatory power characteristic of diabetic sugar, it showed a very slight lævorotation. The addition of 1 gram of sulphonal per litre to urine quite free from sugar gives precisely the same reduction of Fehling's solution.

C. H. B.

**Amount of Iron in Urine.** By LOUIS LAPICQUE (*Bull. Soc. Chim.*, 1895, [3], 13, 281—285).—To estimate iron in urine, a sufficient quantity (200—300 c.c.) is evaporated to dryness with a small amount of nitric acid, and the residue incinerated; the ash is then extracted with hydrochloric acid, and the iron precipitated as phosphate in acetic acid solution, the phosphates of the alkaline earths being thus eliminated. The phosphate of iron is then dissolved in nitrosulphuric acid, and the iron estimated colorimetrically with thiocyanate. The test analyses quoted are satisfactory. Examination of various urines, both healthy and pathological, by this process showed the presence of traces only of iron; the sole exception was that of the urine of a healthy man, which contained 0.6 milligram per litre. JN. W.

**Acetonuria.** By ERNST BECKER and EMILIO PARLATO (*Virchow's Archiv*, 1895, 140, 1—22).—In healthy men, after narcosis, acetonuria is a frequent symptom. It lasts from a few hours to several days; this was very marked in a case of bromether intoxication. It is evidence of increased proteid metabolism.

The estimation of the acetone was effected as follows. 200 c.c. of urine was treated in a flask with 1 c.c. of phosphoric acid and distilled, a stream of air passing the while over the liquid at the end of the distillation. The distillate, after treatment with powdered calcium oxide to remove carbonic anhydride, was brought directly into the flask of Geissler's vaporimeter, the tension was estimated, and the percentage of acetone thus calculated for the original quantity of urine. W. D. H.

**Physiological Action of Carbonic Oxide.** By JOHN S. HALDANE (*J. Physiol.*, 1895, 18, 201—217).—The poisonous action of carbonic oxide diminishes as the oxygen tension increases, and *vice versa*; at a tension of 2 atmos. of oxygen, the poisonous action is abolished in the case of mice. The disappearance of the poisonous action is due to the fact that at high oxygen tensions the animals can dispense entirely with the oxygen-carrying function of hæmoglobin, the oxygen being contained in the plasma. The poisonous action of carbonic oxide is entirely due to its power of combining with the hæmoglobin of the red corpuscles, and so putting them out of action as oxygen carriers.

W. D. H.

**Toxicological Properties of Hydroxylamine.** By ADALBERTO PASQUALI (*Chem. Centr.*, 1894, ii, 957—958; from *Boll. Chim. Farm.*, 1894, 19).—See this vol., ii, 413.

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### Chemistry of Vegetable Physiology and Agriculture.

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**The Glucosazone from Sumach and from Vallonia.** By CARL BOETTINGER (*Arch. Pharm.*, 1895, **233**, 125—127; compare *Abstr.*, 1891, 70).—The author finds that the osazones of the sugars obtained from Sumach and from Vallonia are identical, and that they agree

in all their properties with the osazone obtained from grape sugar. By warming a mixture of glucose and glyoxylic acid, the author has obtained a condensation product of the acetal type, this is being subjected to further examination. J. J. S.

**A Crystalline Constituent of *Basanacantha Spinosa*, Var. *Ferox*, Schum.** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1895, 233, 1—5).—By treating the leaves and bark of *Basanacantha Spinosa*, var. *ferox*, Schum. with alcohol, the author has succeeded in extracting about 2 per cent. of mannitol; the alcoholic solution was evaporated, the residue extracted with water, and the solution precipitated with lead acetate. The filtrate, after the lead had been removed by means of hydrogen sulphide, was evaporated to a syrup, which, when cold, set to a mass of crystals of mannitol.

The author cannot confirm Kwasnik's statement (Abstr., 1892, 1509) that pure mannitol reduces Fehling's solution slightly after boiling or long standing. It does, however, give a silver mirror with ammoniacal silver nitrate. J. J. S.

**The Occurrence of Hesperidin in *Folia Bucco*.** By P. ZENETTI (*Arch. Pharm.*, 1895, 233, 104—111).—The author finds that there is a considerable quantity of hesperidin in the dried leaves of *Diosma alba* and of *Folia bucco*. When the dried leaves are placed in any liquid, the outer epidermal layer becomes separated from the inner, and the space thus formed between the two layers is seen to be filled with yellowish-brown crystals of hesperidin of various shapes.

J. J. S.

**Presence of Chitin in the Cellular Membrane of Mushrooms.** By EUGÈNE GILSON (*Compt. rend.*, 1895, 120, 1000—1002).—When mushrooms (*Agaricus campestris*) are treated successively with dilute sodium hydroxide solution, boiling dilute sulphuric acid, alcohol, and ether, a white substance is left, which, when dried, becomes hard and compact and acquires a horny appearance and structure; its composition is C, 46.11; H, 6.98; N, 6.17; which agrees very closely with the analyses of chitin by Schmidt, Stadeler, Lehman, and Ledderhose, and the substance has all the properties of chitin. It is insoluble in all solvents except concentrated acids, and, when treated with hot concentrated hydrochloric acid, it yields crystals of glucosamine hydrochloride. When heated with potassium hydroxide at 180°, it yields mycosin.

The same substance is obtained from *Amanita muscaria*, *Cantharellus cibarius*, *Hypholoma fasciculare*, *Polyporus officinalis*, *Polyporus fumosus*, *Russula*, *Boletus*, *Tricholoma*, *Bovista*, and *Claviceps purpurea*.

It would seem that chitin plays the same part in mushrooms as cellulose does in all the phanerogams and many of the cryptogams, and constitutes the chief part of the cellular membrane, in which it is associated, however, with carbohydrates analogous to or identical with those found in phanerogams. C. H. B.

**Glyoxylic acid in Green Fruits.** By HEINRICH BRUNNER and ERNEST CHUARD (*Bull. Soc. Chim.*, 1895, [3], 13, 126—128).—Replying to Ordonneau (*Abstr.*, 1892, 589), the authors cannot accept his view that the glyoxylic acid which they isolated, and the glycollic acid which Erlenmeyer isolated from various plants, were none other than his tartromalic acid. In the first place, Ordonneau dealt only with grapes, and with wine residues, whilst the authors examined other fruits, as well as the leaves and buds of plants; and, in the second place, Ordonneau's acid is not capable of reducing ammoniacal silver solutions in the cold, as was, in every case, the acid isolated by the authors, which, therefore, could be none other than glyoxylic acid.

The view that the carbonic acid undergoes gradual reduction during the growth of the fruit is confirmed by the isolation of glyoxylic and glycollic acids from the unripe fruit, as the successive products must be formic, oxalic, glyoxylic, glycollic, succinic, and malic acids, &c. According to this view, also, the glyoxylic acid should gradually disappear as the plant ripens, and this has been proved to be the case.

JN. W.

**Mid-European Nut Galls and *Scrophularia Nodosa* L.** By F. KOCH (*Arch. Pharm.*, 1895, 233, 48—99).—Fresh nut galls, gathered in the beginning of the autumn, 1893, were subjected to examination, with the following results.

Moisture .....	85·71 per cent.
Vegetable tissue.....	11·39 „
Nitrogen .....	0·21 „
Ash .....	0·197 „

The ash had the following composition.

SiO <sub>2</sub> .....	17·79 per cent.
P <sub>2</sub> O <sub>5</sub> .....	32·38 „
CaO .....	5·17 „
SO <sub>3</sub> .....	24·82 „
H <sub>2</sub> O .....	15·65 „

The sugar and tannin were estimated in two different lots of galls: (1) ripe galls, gathered in January; (2) unripe galls, gathered in September. The percentages given refer to the dried, and not to the fresh, moist galls.

	(1).	(2).
Sugar.....	51·81 per cent.	21·47 per cent.
Tannin.....	14·85 „	16·87 „

The galls were finally extracted with (1) petroleum ether, (2) ether, (3) alcohol, and (4) water, in the order given. From the combined petroleum and ethereal extracts, a white substance was obtained, which the author terms *gallocerin*, as it very much resembles the cerin of John, of Chevreul, and of Wittstein. After recrystallisation from alcohol, it forms feathery clusters of crystals, which melt at 173°. It apparently has the composition C<sub>19</sub>H<sub>31</sub>O<sub>2</sub> or C<sub>20</sub>H<sub>36</sub>O<sub>2</sub>, and is

remarkably indifferent towards most reagents, it yields an amorphous monobromo-derivative, however, when treated with bromine, and is decomposed into a mixture of two acids when boiled with potash.

The alcoholic extract yielded tannin and gallic acid, together with a mixture of sugars, from which dextrose was isolated in the pure form; but no characteristic substance could be isolated from the aqueous extract.

*Scrophularia nodosa*.—The ash from the roots contains potassium, sodium, calcium, magnesium, iron, manganese, chlorine, phosphoric acid, and silica.

The ethereal extract yielded butyric and cinnamic acid, together with lecithin; the latter was identified by its decomposition into choline, phosphoric, palmitic, and oleic acids.

From the alcoholic extract, the author has obtained: (1) A resin, which, when hydrolysed, yielded cinnamic acid. (2) Caffetannic acid (compare Hlasiwetz, *Annalen*, **142**, 220; Kunz-Krause, *Abstr.*, 1893, ii, 327), which, when hydrolysed, gave dihydroxycinnamic acid and a sugar, apparently dextrose. (3) A sugar which could not be obtained in the crystalline form, but which seems to be dextrose. (4) Choline. The author states that the scrophularin of Walz (*Jahresber. Fortsch. Chem.*, 1853, 567) does not exist, that Walz's scrophularosamine is palmitic acid, and his scrophularacin is cinnamic acid. No characteristic compounds could be obtained from the aqueous extract, but the author states that dulcite is not present (compare Eichler).

J. J. S.

**Effect of Arsenic on Vegetation.** By AUG. LYTTKENS (*Bied. Centr.*, 1895, **24**, 352; from *Kgl. landtbruksakad. handl. o. tidskr.*, 1894, **33**, 317—320).—Experiments in which barley was grown in garden soil, and in the same soil to which 0.005 and 0.01 per cent. of arsenious acid (as potassium salt) was added, showed that those quantities of arsenic caused slow and feeble growth, and a blue-green colour.

An examination of 75 samples of superphosphates received at Halmstad showed 40 per cent. to be strongly arsenical ( $\text{As}_2\text{O}_3$  = about 0.1 per cent.), 15 per cent. slightly arsenical, and the rest free from arsenic. The strongly arsenical samples of known origin were foreign.

N. H. J. M.

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### Analytical Chemistry.

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**Sources of Error in Alkalimetry.** By P. DOBRINER (*Zeit. angew. Chem.*, 1895, 259—262).—The author states that if a sample of any acid is titrated with standard soda under exactly the same conditions as when doing the check experiment, no sources of error are introduced by the presence of a small quantity of carbonate in the alkali.

L. DE K



**Luteol, a new Indicator.** By WILHELM AUTENRIETH (*Arch. Pharm.*, 1895, **233**, 43—48).—See this vol., i, 572.

**Modification of Soxhlet's Extraction Apparatus.** By A. PHILIPS (*Ber.*, 1895, **28**, 1475). The side tube of the ordinary Soxhlet, which conveys the vapour of the liquid to the condenser, is replaced by an annular space which surrounds the extraction space into which the liquid drops after condensation. This acts as a vapour jacket, and keeps the extracting liquid at a temperature near its boiling point throughout the extraction, a considerable amount of time being thus saved.  
A. H.

**Estimation of Halogens by Carius' Method: Application of Volhard's Modification.** By FRITZ W. KÜSTER (*Annalen*, 1895, **285**, 340—348).—The author describes in detail the conditions under which halogen determinations are carried out in the Marburg laboratory. By enveloping the tube in blotting paper, risk of explosion is minimised, and the temperature may be raised as rapidly as possible to 320—340°, at which most substances are completely decomposed after an exposure of two hours. On diluting the contents of the tube with water, it suffices, when chlorine is being estimated, to allow the liquid to remain for a short time on the water bath, but in the case of bromine and iodine more systematic treatment with boiling water is necessary; the silver haloid is then transferred to a Gooch crucible, which is dried for 1½ hour in the vapour of boiling xylene.

In Volhard's modification of Carius' method, a known quantity of silver nitrate is employed, and after removing the silver haloid, the excess of silver is determined by titration with ammonium thiocyanate. The author, in applying this modification, has found it untrustworthy, titration invariably indicating the presence of silver in too small a quantity. Careful quantitative experiments have traced this discrepancy to the familiar brown stain acquired by tubes employed in halogen determinations, the coloration being due to silver, which is taken up by the glass in quantities which increase with the temperature and duration of heating.  
M. O. F.

**Estimation of Sulphur in Pyrites.** By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1895, **17**, 397—401).—A reply to Lunge (this vol., ii, 291), stating that the author's modifications of his process are absolutely necessary to get accurate results.  
L. DE K.

**Estimation of Sulphur in Iron and Steel.** By LOUIS CAMPREDON (*Compt. rend.*, 1895, **120**, 1051—1054).—2·5 to 10·0 grams of the metal is dissolved in 100 c.c. of sulphuric acid (1 : 5) or hydrochloric acid (1 : 3) in a flask previously filled with carbonic anhydride, and connected with two apparatus supplying hydrogen and carbonic anhydride respectively. The mixture of gas evolved by the action of the acid on the metal, with the hydrogen and the carbonic anhydride, is passed through a porcelain tube heated to orange redness or an incipient white heat, and all the gaseous sulphur compounds are thus

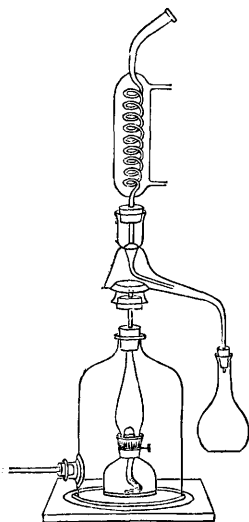
converted into hydrogen sulphide. The gas is then passed into 100 c.c. of a slightly acidified solution of zinc acetate, and the zinc sulphide that is precipitated is mixed with standard iodine solution, the excess of the latter being ascertained by means of standard sodium thiosulphate solution.

The zinc acetate solution is prepared by dissolving 10 grams of zinc oxide in 25 c.c. of glacial acetic acid, diluting to about 500 c.c., adding sufficient ammonia to redissolve the precipitate which forms at first, and then slightly acidifying with acetic acid.

To prepare the iodine solution, 7.9 grams of purified iodine, together with 25 grams of potassium iodide, is dissolved in 1000 c.c. of water, 1 c.c. = 0.001 gram of sulphur. The thiosulphate solution contains 10 grams of sodium thiosulphate and 2 grams of ammonium carbonate per litre.

C. H. B.

**Estimation of Sulphur in Petroleum.** By FRIEDRICH HEUSLER (*Zeit. angew. Chem.*, 1895, 285—286).—The apparatus (see illustration) consists of four parts: a small petroleum lamp with its chimney, a reflux condenser, and a special connecting piece which causes the condensed liquid to run into a receiver by means of a small funnel. The wide top end of the coiled cooling tube is closed by a doubly-perforated stopper; through one opening passes a tube connected with a suitable aspirator; through the other one is introduced a capillary angular syphon through which drops a solution of potassium permanganate. This solution first runs over a pad of glass wool contained in the wide upper tube. If the sample is somewhat rich in sulphur, the permanganate will sometimes be rapidly decolorised; in this case it probably does not run in quickly enough.



To carry out an experiment, the lamp (without its glass) is taken out, filled with about 20—30 grams of the sample, and weighed. Then the suction pump and the capillary syphon are put in action, and when the permanganate solution has moistened the whole of the coil, the condenser and connecting piece are lifted up, and the

lighted lamp is fixed to the lamp-glass, which is attached to the top of the bell-jar by means of a perforated cork. The bell-jar is put on to a greased glass plate, the cooler and connecting piece are lowered, and the latter is connected by a glass tube and cork with the jar. With a little practice, it will be found easy to so regulate the force of the air current that complete combustion takes place; once set going satisfactorily, the lamp will burn 12 hours, or even longer. The lamp is then re-weighed, the loss in weight representing the amount of oil burned. The condenser, connecting piece, and lamp-glass are

all rinsed with water, and the washings added to the liquid in the receiver, which should still contain excess of permanganate. After boiling with hydrochloric acid and filtering, barium chloride is added.

L. DE K.

**Standardising Sulphuric acid.** By F. S. SHIVER (*J. Amer. Chem. Soc.*, 1895, 17, 351—354).—Weinig (Abstr., 1892, ii, 145) has recommended standardising sulphuric acid by neutralising it with ammonia, evaporating to dryness, and finally weighing the ammonium sulphate.

The author states that excellent results may be obtained by this process, but as some ammonia is liberated during the evaporation, it is advisable to moisten the dry residue with ammonia of 0.96 sp. gr., and to again evaporate to dryness. Before weighing, the ammonium sulphate is dried at 110—120°.

L. DE K.

**Assay of Fuming Sulphuric acid.** By GEORG LUNGE (*Zeit. angew. Chem.*, 1895, 221—222).—The total acidity of fuming sulphuric acid is generally estimated by means of standard soda, from which is then deducted the acidity due to the sulphurous acid, which is estimated as usual with standard iodine. This process may, however, lead to grave errors.

The indicator used is not a matter of indifference; phenolphthaleïn is not to be recommended, as the soda nearly always contains carbonate, and litmus is out of the question on account of the sulphurous acid. The only good indicator is methyl-orange, but it must be remembered that when using this reagent, neutrality is reached, not when the whole of the sulphurous acid is converted into the neutral sulphite, but as soon as the acid sulphite is formed.

L. DE K.

**Chemical and Toxicological Properties of Hydroxylamine.** By ADALBERTO PASQUALI (*Chem. Centr.*, 1894, ii, 957—958; from *Boll. Chem. Farm.*, 1894, 19).—Angeli's test for hydroxylamine with sodium hydroxide and nitroprusside is well known. Another delicate test is to boil the solution of hydroxylamine hydrochloride with copper sulphate, when nitrous oxide is evolved and cuprous chloride precipitated. Lead peroxide is changed into lead hydroxide, or lead chloride or sulphate also accompanied by evolution of nitrous oxide, whilst the solution contains lead nitrate and nitrite. Magnesium in contact with solutions of hydroxylamine liberates hydrogen. Aqueous potash and carbon bisulphide first give a yellow, and then an orange, liquid; basic lead acetate, or lead hydroxide substituted for the potash, give, on warming, a canary-yellow colour, which fades on adding acids, but turns black with potash. As hydroxylamine does not affect the usual indicators, its salts may be titrated best in presence of phenolphthaleïn with standard alkali. A new volumetric process is based on the fact that hydroxylamine decolorises an ammoniacal solution of copper sulphate.

As regards its poisonous character, the author found that it only acts in large doses: 7.75 grams of the hydrochloride given to a dog in small portions during nine days did not affect the animal, but 3 grams administered all at once, caused death. There is no difficulty in finding

traces of the poison in bodies after death even after the lapse of a month.

When hydroxylamine poisoning is suspected, the urine should be tested for nitrous acid.

L. DE K.

**Volumetric Estimation of Phosphorus in Steel and Cast Iron.** By WILLIAM A. NOYES and J. S. ROYSE (*J. Amer. Chem. Soc.*, 1895, 129—137).—Two grams of the sample is put into a 500 c.c. flask, 50 c.c. of nitric acid added, and heat applied until solution is complete; 10 c.c. of a 1·25 per cent. solution of potassium permanganate is then poured in, and the boiling continued until the pink colour disappears. Ferrous sulphate is added, with shaking, until the liquid clears, and, after cooling to 50°, 8 c.c. of ammonia of 0·9 sp. gr. is added, the stopper inserted, and the precipitate redissolved by shaking. The solution is then heated as many degrees above or below 60° as the molybdate solution (100 grams of molybdic acid, 400 c.c. of ammonia, 1000 c.c. of nitric acid, sp. gr. 1·2) is below or above 27°; 60 c.c. of this solution is added, the stopper is inserted, and the whole shaken, best with a machine, for five minutes. After another five minutes, the molybdate precipitate is collected on a filter of fine texture, and washed with solution of hydrogen ammonium sulphate (27·5 c.c. of ammonia of 0·96, 24 c.c. of sulphuric acid, and 500 c.c. of water) until the washings are no longer coloured by hydrogen sulphide. The precipitate is now dissolved in 12 c.c. of ammonia of sp. gr. 0·96, the filter is washed with 100 c.c. of water, 80 c.c. more water is added, and then 10 c.c. of sulphuric acid.

The solution is passed through a Jones' reductor containing zinc, no air being allowed to pass through during reduction or the washing, and the filtrate is at once titrated with permanganate. The phosphorus equivalent is found by multiplying the iron equivalent of the permanganate by 0·01538.

L. DE K.

**Estimation of Phosphoric acid by means of Ammonium Molybdate.** By HANNS VON JÜPTNER (*Chem. Centr.*, 1894, ii, 813—814; from *Österr. Zeit. Berg. Hütt.*, 42, 471—473).—The author has found that tartaric acid even in large excess does not prevent the complete precipitation of phosphoric acid by molybdate solution. The addition of tartaric acid to the molybdate solution or to the phosphate is therefore to be recommended to prevent the contamination of the yellow precipitate with ferric compounds.

L. DE K.

**Estimation of Phosphoric acid by the Molybdic acid-Magnesia Process.** By RUDOLF DE ROODE (*J. Amer. Chem. Soc.*, 1895, 43—46).—The author has proved that at 65° the precipitation of phosphoric acid by the ordinary molybdate solution is complete in five minutes. In analysing phosphates, the author has found it advantageous to add a definite quantity of sodium phosphate solution, the results then being more accurate. The weight of magnesium pyrophosphate yielded by this solution is, of course, deducted from the actual weight. Or, the ignited magnesia precipitate is

dissolved in nitric acid and reprecipitated with molybdate solution, and finally with magnesia mixture; in this case, there is no need for adding sodium phosphate. The author also recommends working on fairly large quantities of substance.

L. DE K.

**Estimation of Phosphoric acid.** By H. PEMBERTON (*J. Amer. Chem. Soc.*, 1895, 178—181).—The molybdate solution should be added slowly so as to get the yellow precipitate in a crystalline and consequently purer condition. The precipitate is best treated according to the volumetric method, which is quite as trustworthy as the gravimetric process. If titrated with standard alkali, the indicator should be phenolphthaleïn, not methyl-orange.

L. DE K.

**Preparation of Thioacetic acid and its Use in Toxicology.** By N. TARUGI (*Gazzetta*, 1895, 25, i, 269—273; compare Schiff and Tarugi, this vol., ii, 84).—The best method of preparing thioacetic acid for analytical purposes is a slight modification of that described by Kekulé and Linnemann (*Annalen*, 123, 278), which consists in cautiously distilling phosphorus pentasulphide (300 grams) with glacial acetic acid (108 grams) over a naked flame from a 2-litre flask, pellets of glass (100 grams) being added to prevent frothing; the thioacetic acid may be collected until the thermometer registers 100°, and after one redistillation—collecting the fraction boiling at 90—95°—is perfectly free from arsenic, and may be at once used in toxicological investigation for the precipitation of arsenic. The acid is dissolved in water (2 parts) with the aid of a little ammonia, and the solution thus obtained is boiled with the arsenical liquid; the arsenic is immediately deposited as sulphide, which is collected and examined in Marsh's apparatus.

W. J. P.

**Separation of Arsenic from other Elements by means of Methylic Alcohol and Hydrogen Chloride.** By CARL FRIEDHEIM and PAUL MICHAELIS (*Ber.*, 1895, 28, 1414—1422).—The authors recommend the use of methylic alcohol instead of ferrous chloride in E. Fischer's method for the estimation of arsenic (*Abstr.*, 1881, 195). The general method of procedure is as follows:—

A distilling flask of about 250 c.c. capacity is used, and is fitted with a ground head which is fused to the condenser; a small separating funnel is also ground into the head, and reaches to the bottom of the flask. The receivers are also united to the condenser by means of ground joints. The solution of the substance to be analysed is placed in the flask, and 50 c.c. of methylic alcohol is added; 20 c.c. of concentrated nitric acid is poured into the first receiver, and the others are moistened with distilled water. The mixture in the flask is then saturated with dry hydrogen chloride, the separating funnel serving to keep the methylic alcohol from running back into the drying bottle; during the operation, the flask is kept cool by means of cold water, and, after the solution is completely saturated with hydrogen chloride, it is heated on the water bath while a slow stream of the gas is kept passing through the liquid. If much arsenic is present the operation must be repeated two or three times. Fresh methylic alcohol is

added by means of the separating funnel, and the saturation and distillation are repeated. The distillate, after all the arsenic has passed over, is poured into a porcelain dish and diluted with water; 20–30 c.c. of concentrated nitric acid is added, and, after the vigorous evolution of chlorine has ceased, the whole is evaporated down on the water bath to about 100 c.c. Another 20–30 c.c. of concentrated nitric acid is added, and the liquid is then evaporated down to dryness; the residue is extracted with water, filtered, and precipitated with magnesia mixture. Details are given (1) of estimations of pure arsenic; (2) of the separation of arsenic and vanadic acid; (3) of the separation of arsenic and molybdic acid; (4) of the estimation of arsenic and tungstic acid.

In order to completely separate arsenic and vanadic acid, it is necessary to reduce the latter to  $V_2O_4$ , by warming for a short time with sulphurous acid, and then to distil in the usual way, as otherwise part of the vanadium passes over with the arsenic.

In order to prevent part of the molybdenum from passing over with the arsenic, it is necessary to dilute the methylic alcohol with water for the first operation. Arsenic acid in the presence of tungstic acid cannot be estimated by this method, as 2–3 per cent. of the arsenic always remain behind in the distilling flask. The author recommends the estimation of the two together by means of mercurous nitrate solution (see Gibbs, *Proc. Amer. Academy*, **16**, 134), then the estimation of the tungsten separately, and the calculation of the arsenic from the difference.

J. J. S.

**Two New Colorimeters for Carbon Estimation.** By WALTER G. McMILLAN (*Chem. Centr.*, 1895, i, 173–174; from *Stahl u. Eisen*, 1894, 1073–1075).—The first apparatus consists of two graduated cylinders, one of these containing the solution to be tested, and the other the standard solution used for comparison; the second cylinder being connected by a side tube with a reservoir containing a float. By depressing the latter, the depth of the column of liquid in the comparison tube can be adjusted so as to correspond in colour with the solution which is being tested. A milk-white stopper is placed level with the zero in each tube, and a movable shutter facilitates the reading of the graduation. In the second form of apparatus, the standard liquid and that for comparison are placed in tubes the upper part of which is expanded in the form of a basin. These are enclosed in a blackened case with a long slit in the bottom, to which light is directed by a reflector, and in each, another tube is made to slide and regulate the depth of liquid. The sliding tubes are provided with an index working on a scale, and to begin with are depressed till the liquid is forced into the basin-like neck of the containing tubes, and a white disc only appears on observation. This is taken as zero. One tube is then raised until a suitable colour and depth of liquid is obtained, and the other is adjusted to correspond.

L. DE K.

**Analysis of Bone-black.** By W. D. HORNE (*J. Amer. Chem. Soc.*, 1895, ii, 51–55).—The author restricts the analysis to the estimation of moisture, carbon, calcium carbonate, sulphate, and sulphide, also

iron and alumina. The analytical details present, on the whole, no novel features. The density is determined by filling a weighed 100 c.c. flask, with sloping sides, with the sample and re-weighing; this gives the sp. gr. of the loose char. The flask is then gently tapped, and more char is added; this gives the sp. gr. of the packed sample.

To determine the relative durability of sample under continued friction, the following test is recommended: 25 grams of the sample between 16—24 grist is thrown on a sieve with circular holes one-fiftieth of an inch in diameter, the sieve shaken backwards and forwards 10 times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron, 4 inches in diameter and 2 inches deep, along with six glazed porcelain marbles, five-sixths of an inch in diameter, and jointly weighing 74.66 grams. The can is now shaken backwards and forwards with a slightly rotatory motion 200 times, the marbles are removed, and the char is again sifted. The increase in the weight of dust will then give an idea as to the quality of the sample.

L. DE K.

**Absorption Apparatus for Elementary Analysis.** By JULIUS BREDT and WILHELM POSTH (*Annalen*, 1895, 285, 385—386).—The authors advocate the employment of soda-lime as a substitute for potassium hydroxide.

M. O. F.

**Estimation of Potash in Kainite.** By RUDOLF DE ROODE (*J. Amer. Chem. Soc.*, 1895, ii, 85).—The author recommends evaporating the aqueous solution of kainite with the addition of platinum chloride, without any attempt at removing sulphates, lime compounds, &c. The residue is first extracted with alcohol to remove the excess of platinum chloride, and then with a solution of ammonium chloride to remove the impurities; a pure potassium platinochloride is thus obtained. The test-analysis was slightly higher than the usual result, but this is only natural, as the new process is not interfered with by occlusion of potash in the various precipitates, or by loss from decrepitation or volatilisation.

L. DE K.

**Estimation of Potash in Manures.** By W. E. GARRIGUES (*J. Amer. Chem. Soc.*, 1895, ii, 47—51).—Ten grams of the sample is well mixed with strong sulphuric acid, in a platinum dish, and the whole is then gradually ignited until all the organic matter has been burnt off. The mass is now powdered, washed into a 500 c.c. flask with 250 c.c. of hot water, boiled for half an hour, and a 10 per cent. solution of barium chloride is cautiously added until no further precipitate is produced. A drop of phenolphthaleïn is introduced, and then, drop by drop, a solution of sodium carbonate until a faint, permanent rose colour is obtained. After cooling, the liquid is diluted to the mark, and 50 c.c. (1 gram) of the filtrate is used for the potash estimation. This is done, as usual, by evaporation with platinum tetrachloride and a drop of hydrochloric acid.

When analysing potash salts, the evaporation with sulphuric acid may be omitted.

L. DE K.

**Estimation of Potassium Sulphate in Wine.** By L. HUGOUNENQ (*J. Pharm.*, 1895, [6], i, 349—354).—The author has proved that wine contains organic sulphur compounds, which afterwards are found in the ash as sulphates, and so increase the quantity of potassium sulphate by 30—40 per cent. To get a correct result, the estimation of the sulphuric acid must be made in the original sample, and not on the acid solution of the ash. The various sugars, tartrates, &c., contained in the wine have no particular influence on the accuracy of the result.

L. DE K.

**Reaction between Zinc Sulphate and Potassium Hydroxide.** By C. E. LINEBERGER (*J. Amer. Chem. Soc.*, 1895, 17, 358—360).—In works on analytical chemistry, it is customary to represent two molecules of potassium hydroxide as necessary to precipitate the zinc from one molecule of zinc sulphate. The precipitate is then supposed to redissolve by adding another two molecules of potash.

The author has experimentally proved that these ideas are quite erroneous, and that the reaction depends on temperature, dilution, and the relative masses of the components. In one experiment, 1.62 mols. of potassium hydroxide were sufficient to completely throw down a molecule of zinc, and in another trial not *two*, but 13.2 mols. of alkali were necessary to redissolve the molecule of zinc hydrate.

L. DE K.

**Volumetric Estimation of Metals.** By HENRI LESCOEUR (*Bull. Soc. Chim.*, 1895, [3], 13, 280—281).—The author has for some years past used a process for the estimation of zinc in presence of free acid very similar to that described by Barthe (this vol., ii, 371), methyl-orange being substituted for the tincture of hollyhock. The precipitate obtained in this modified process is not, however, a basic sulphate, but the pure oxide of the metal.

JN. W.

**Estimation of Lead.** By ANDREAS KREICHGAUER (*Zeit. anorg. Chem.*, 1895, 9, 89—125; see also Abstr., 1894, ii, 217).—The paper contains a critical account of the electrolytic estimation of lead, and the results obtained with three different natural sulphides of lead, when analysed by the electrolytic method, by precipitation with bromine, and as sulphate, are compared. The precipitation with bromine is most convenient when the ores contain much antimony or zinc. The electrolytic method is adapted for products containing only small quantities of antimony, and especially when the product can be dissolved directly in nitric acid, and this process is generally the most accurate. The precipitation as sulphate is only advantageously employed when lead alone is present.

E. C. R.

**Quantitative Analysis of Galena.** By PAUL JANNASCH and H. KAMMERER (*Ber.*, 1895, 28, 1409—1411).—The authors recommend the following method for the analysis of galena. 0.7—0.75 gram of the finely powdered mineral is moistened with dilute nitric acid, and allowed to remain for several minutes, 10 c.c. of concentrated acid is then added, and the whole is heated on the water bath, and evaporated; nitric acid and water are then added, together with



10–15 drops of bromine, and the mixture is heated with continual stirring until all the sulphur is oxidised to sulphuric acid. In order to decompose any bromate which may be formed, the mixture should be evaporated to dryness three times with concentrated nitric acid. The residue is boiled with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and filtered from the insoluble residue ( $\text{SiO}_2$ , &c.), which is ignited and weighed. To estimate the lead, the filtrate is heated to boiling, and the clear solution poured at once into a mixture of 25 c.c. of water, 50 c.c. of hydrogen peroxide, and 50 c.c. of concentrated ammonia; the lead is thus thrown down as a yellowish-red, slightly crystalline precipitate, the composition of which will be determined later. The mixture is allowed to remain for several hours, with occasional stirring, the precipitate is then collected, washed with cold water, dried, and weighed in a platinum crucible as lead oxide. The filtrate is evaporated down, until the smell of ammonia has disappeared; 5 c.c. of concentrated hydrochloric acid and 5 c.c. of alcohol are added, the mixture again warmed, in order to destroy any persulphate which may be present, and the sulphuric acid is then precipitated by means of barium chloride. Impurities such as copper, nickel, zinc, and arsenic can be estimated in the filtrate from the barium sulphate. J. J. S.

**Wet Copper Assay.** By R. S. DULIN (*J. Amer. Chem. Soc.*, 1895, 17, 346–351).—The most popular (American) assaying processes in the wet way are the electrolytic method, and the process by which the copper is precipitated by potassium iodide and the liberated iodine titrated, but these processes can only be employed in the absence of interfering metals or acids. The time-honoured cyanide process gives, however, excellent results, provided the copper is first precipitated with aluminium.

The copper ore is treated according to the directions given in Furmen's Manual of Assaying, the resulting solution being practically free from lead and silver; when boiled with strips of aluminium foil, the copper is completely precipitated, and if the boiling is then stopped at once, scarcely any cadmium will come down. The copper deposit is washed, dissolved in nitric acid, mixed with excess of ammonia, and titrated with potassium cyanide solution; in standardising the latter, as nearly as possible the same amount of copper, nitric acid, ammonia, &c., should be used in order to get trustworthy results.

L. DE K.

**Quantitative Separation of Metals in Alkaline Solution by Hydrogen Peroxide.** By CARL ENGELS (*Zeit. anorg. Chem.*, 1895, 9, 78).—Regarding the paper by P. Jannasch and A. Röttgen with this title (this vol., ii, 331), the author states that he has been for some time engaged in the electrolytic separation of manganese from iron and copper in the presence of hydrogen peroxide and an organic compound. 0.5 gram  $\text{MnO}_2$  can be estimated quantitatively by this method in one hour.

E. C. R.

**Electrolytic Estimation of Manganese.** By MAX GRÖGER (*Zeit. angew. Chem.*, 1895, 253–254).—Electrolytically deposited manganese

peroxide has, according to Rüdorff, the composition,  $\text{MnO}_2, \text{H}_2\text{O}$ , when dried at  $60^\circ$ ; using this formula, about 99 per cent. of manganese present is recovered during an analysis. The author has, however, proved that the precipitated manganese is not entirely in the state of dioxide, and if estimating it by means of potassium iodide and sodium thiosulphate, only 94—96 per cent. of the manganese will be found.

L. DE K.

**Methods for Estimating Manganese.** By W. S. THOMAS (*J. Amer. Chem. Soc.*, 1895, **17**, 341—346).—The author has investigated some volumetric methods for estimating manganese with the object of finding out which process is most suitable for technical purposes.

The conclusion is, that the best method is the one proposed by Volhard, namely, titration of the manganous salt by means of potassium permanganate in presence of zinc oxide. Low's oxalic acid process, although theoretically perfect, has entirely failed in the author's hands.

L. DE K.

**Estimation of Iron in Ores, Slags, &c.** By HANS VON JÜPTNER (*Chem. Centr.*, 1894, ii, 815; from *Österr. Zeit. Berg Hütt.*, **42**, 469—470).—0.5 gram of the sample is mixed with 1 gram of magnesium powder and ignited for 5—10 minutes in a covered porcelain crucible; if the substance is very rich in ferrous oxide, 4—6 grams of magnesium should be used. The magnesium should be tested as to the amount of iron it contains.

The contents of the crucible is dissolved in dilute sulphuric acid and the iron estimated with standard permanganate.

L. DE K.

**Zimmermann-Reinhardt's Method for Estimating Iron in Iron Ores.** By C. T. MIXER and H. W. DU BOIS (*J. Amer. Chem. Soc.*, 1895, **17**, 405—411).—The ore is dissolved in hot hydrochloric acid with the addition of stannous chloride, solution being complete in a few minutes. The excess of stannous chloride is removed by the addition of mercuric chloride, and the iron is then at once titrated with permanganate solution. To prevent injurious action of the hydrochloric acid on the permanganate, a solution of manganous sulphate also containing sulphuric and phosphoric acid is added before titration. The permanganate is checked by means of a standard iron ore, the composition of which has been ascertained in a variety of ways.

The authors, after a good many trials, strongly recommend this method for technical purposes.

L. DE K.

**Analysis of Steel.** By H. K. BAMBER (*Chem. Centr.*, 1894, ii, 815; from *Stahl u. Eisen*, **14**, 872).—The sample is dissolved in dilute nitric acid, nearly neutralised with sodium hydroxide, and the liquid evaporated to dryness; the mass is then treated with 50 c.c. of 10 per cent. aqueous soda, again evaporated to dryness, and powdered. The powder is lixiviated with 0.5 per cent. aqueous soda, which then contains the various minor constituents such as phosphorus, arsenic, sulphur, chromium, vanadium, molybdenum, &c.

L. DE K.

**Estimation of Iron in Urine.** By LOUIS LAPICQUE (*Bull. Soc. Chim.*, 1895, [3], 13, 281—285).—See this vol., ii, 407.

**Estimation of Nickel in Nickel-Steel.** By EDWARD D. CAMPBELL and W. H. ANDREWS (*J. Amer. Chem. Soc.*, 1895, ii, 125—129).—*Preliminary Treatment.*—One gram of the sample is boiled in a 500 c.c. Erlenmeyer flask with 25 c.c. of nitric acid (sp. gr. 1.20) until dissolved, meanwhile, 13 grams of sodium pyrophosphate is dissolved in 75 c.c. of warm water, filtered, and added to the cooled nitric acid solution. A 20 per cent. solution of sodium carbonate is now slowly poured in until the ferric pyrophosphate has just dissolved, and the liquid attains a dull, olive-green colour; excess of soda, betraying itself by a red colour, must be carefully avoided. The liquid is now filtered through asbestos into a 500 c.c. Erlenmeyer flask, a solution of 2 grams of potassium xanthate in 25 c.c. of water is added, and the flask is stoppered and well shaken for about 10 minutes. The nickel is completely precipitated as xanthate, together with any copper, but is perfectly free from manganese and almost free from iron; the precipitate, collected on an asbestos filter, must be washed with a 1 per cent. solution of the reagent, which, in solution, does not keep more than 15 minutes.

The precipitate is dissolved off the filter by allowing 20 c.c. of nitric acid (10 c.c. of water, 10 c.c. of fuming acid) to slowly drop on to it; the filter is first washed a few times with hot water, then with 5 c.c. of dilute sulphuric acid (2—3), and finally again with hot water. The solution is now rapidly boiled in an Erlenmeyer flask until the nitric acid is completely expelled, and fumes of sulphuric acid begin to be visible. After cooling, the residue is dissolved in 25 c.c. of water, heated nearly to boiling, a current of hydrogen sulphide passed through it to precipitate the copper, and the whole filtered. The filtrate is boiled to expel the gas, and the iron, oxidised by means of a few drops of hydrogen peroxide, or by a few particles of sodium dioxide, is at once precipitated by ammonia; the precipitate must, however, after washing, be redissolved in 5 c.c. of the dilute sulphuric acid, and again precipitated hot with ammonia so as to completely free it from nickel. In the united filtrates, the nickel may then be determined either by electrolysis or by titration.

*Electrolytically.*—The solution, mixed with 30 c.c. of 10 per cent. ordinary sodium phosphate and 25 c.c. of strong ammonia, is diluted to about 175 c.c., and placed in a platinum dish of 200 c.c. capacity; the nickel is then deposited on the platinum by means of a current of 0.14 ampère per 100 sq. cm. area of the dish, the electrodes being about 0.5 cm. apart.

*Volumetrically.*—To the liquid is added 5 c.c. of a solution of silver nitrate (0.05 per cent.), then 5 c.c. of a 2 per cent. solution of potassium iodide; solution of potassium cyanide (0.5 per cent.) is now run in until all the nickel has passed into double cyanide, which is indicated by the disappearance of the silver iodide. The cyanide solution is standardised by means of pure nickel wire, and a blank experiment is made to ascertain the amount of cyanide required to dissolve the silver iodide.

L. DE K.

**Separation of Metals with a Current of Carbonic Anhydride containing Bromine.** By PAUL JANNASCH, ED. ROSE, and R. NIEDERHOFHEIM (*Zeit. anorg. Chem.*, 1895, **9**, 194–204).—*Separation of Bismuth and Cobalt.*—For the test experiment, a mixture of metallic bismuth with cobalt ammonium sulphate was employed. A weighed quantity of the finely powdered substance, dried in a current of carbonic anhydride, whereby the greater part of the ammonium salt is eliminated, is mixed with about 10 times its weight of pure sulphur, heated in a current of dry hydrogen sulphide, and allowed to cool. The product is again heated with sulphur, and, after the excess of sulphur has sublimed, it is allowed to cool, and is treated with a current of dry carbonic anhydride saturated with bromine; meanwhile the tube containing the mixture is cautiously heated. Sulphur bromide sublimes at first, and then bismuth bromide, and the temperature must be regulated so that no lustrous spangles of cobalt bromide are formed; the volatile products are collected in dilute nitric acid. The green residue of cobalt bromide is dissolved in water, except a small black residue, which requires nitric acid to dissolve it; it contains no bismuth. The solution, heated to boiling, is precipitated with sodium hydroxide, and the cobalt weighed either as  $\text{Co}_3\text{O}_4$  or as metallic cobalt. The nitric acid solution containing the bismuth is evaporated to dryness on the water bath, the residue dissolved in dilute nitric acid, and the bismuth precipitated with an excess of ammonia and hydrogen peroxide. The results obtained are accurate.

The separation of bismuth and nickel is performed in the same way as above. It is very difficult to dissolve the residual crystalline nickel compound in water, but it easily dissolves on the addition of acid.

*Separation of Tin and Antimony from Lead and Copper.*—The method is similar to that described above. The mixture of metals is weighed into a porcelain boat and heated in a tube of hard glass. Before treating with bromine, the sample to be analysed is heated with sulphur containing iodine. The bromine must be free from chlorine and water, and the carbonic anhydride from hydrochloric acid. In the separation of tin and lead, the residue of lead bromide can be weighed as such; it should give a clear solution in fresh chlorine water. In the separation of tin and copper, the solution containing the tin is first evaporated to dryness on the water bath, and is then heated in an air bath to drive off the sulphuric acid; the tin oxide obtained is heated until the weight is constant. The residue of copper, which is not pure cupric bromide, but contains cuprous bromide, is dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue of nitrate ignited, and weighed; or the nitric acid solution is at once precipitated with sodium hydroxide. The separation of antimony from lead is very similar to that of tin from lead, but great care must be taken that no antimony sulphide is volatilised during the treatment with sulphur. The antimony solution is evaporated and freed from sulphuric acid as in the case of tin, it is then evaporated to dryness two or three times with fuming nitric acid, ignited, and the antimony weighed as antimony metantimoniate. Or the antimony is precipitated directly from the nitric acid solution

as sulphide, the precipitate washed with a solution of ammonium nitrate containing hydrogen sulphide, dried at 80—90°, and then treated with fuming nitric acid, and the antimony weighed as dioxide. The separation of antimony and copper is performed in a similar way.

E. C. R.

**Quantitative Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide.**—12th Paper. By PAUL JANNASCH and H. KAMMERER (*Ber.*, 1895, 28, 1407—1409).—(1) *Separation of Manganese and Silver.*—Silver nitrate (0.7—0.8 gram) and manganese-ammonium sulphate (0.7 gram) are dissolved in a mixture of water (10 c.c.) and concentrated nitric acid (10 c.c.); the solution thus obtained is poured into a mixture of water (20 c.c.), hydrogen peroxide (50 c.c.) and concentrated ammonia (40 c.c.) and the whole is heated on the water bath during 10—12 minutes. The precipitate is collected and washed, first with a mixture of water (8 parts by vol.), hydrogen peroxide (17 parts) and ammonia (17 parts), and finally with hot water. After ignition, the manganese is weighed as  $Mn_3O_4$ . The filtrate is heated on the water bath until the smell of ammonia has disappeared, nitric acid is added and the silver estimated in the usual way as chloride.

(2) *Separation of Bismuth and Cobalt.*—Cobalt ammonium sulphate (0.5 gram) and metallic bismuth (0.35 gram) are heated on the water bath with concentrated nitric acid (10 c.c.) and water (10 c.c.), until all is dissolved. The solution, after the addition of concentrated nitric acid (10 c.c.), is poured into a freshly prepared mixture of water (20 c.c.), hydrogen peroxide (50 c.c.), and concentrated ammonia (50 c.c.). The bismuth precipitate, which still contains a trace of cobalt, is collected and washed, first with a mixture of water, hydrogen peroxide and ammonia (see above), then with dilute ammonia, and finally with hot water. It is now dissolved in hot, dilute nitric acid, and concentrated acid is added in order to make up the total amount of concentrated acid present to 20 c.c. The precipitation is again repeated, and after washing as before, the precipitate is dried at 90°, and ignited and weighed in a platinum crucible as bismuth oxide. The filtrate containing all the cobalt is evaporated to dryness, and the residue heated in an air bath to drive off all ammonium salts; it is then dissolved in water to which hydrogen peroxide and a few drops of hydrochloric acid have been added, the solution heated to boiling, and the cobalt precipitated by the addition of a slight excess of pure sodium hydroxide, together with bromine; the precipitate is dried, ignited and weighed as  $Co_3O_4$ . The cobalt may also be directly precipitated from the ammoniacal filtrate by means of ammonium sulphide.

J. J. S.

**Estimation of Paraffin in Crude Anthracene.** By FRIEDRICH HEUSLER and JOS. HERDE (*Zeit. angew. Chem.*, 1895, 253).—The process is based on the fact observed by the authors that all the constituents of crude anthracene, paraffin excepted, are soluble in fuming nitric acid.

Two grams of the sample is put into a 150 c.c. flask, cooled in iced water, and very gradually mixed with 25 c.c. of fuming nitric acid; the mixture is then heated for a while on the water bath until the paraffin has melted, and again cooled. The solid mass is now collected on an asbestos filter, and after being washed with fuming nitric acid until this no longer becomes milky on adding water, the acid is removed by washing with water. The paraffin is first rinsed with alcohol into a weighed porcelain dish, and the spirit evaporated; in the meantime, the remaining paraffin is dissolved in hot ether, and this solution is also evaporated in the same dish. Before weighing, the paraffin is finally dried at 105—110° for half an hour.

L. DE K.

**Detection of Potassium Cyanate in small quantity, in Potassium Cyanide.** By EDWARD A. SCHNEIDER (*Ber.*, 1895, 28, 1540—1541).—The method is based on the formation of the deep-blue potassio-cobalt cyanate,  $\text{Co}(\text{CNO})_4 \cdot 2\text{KCNO}$ . The potassium cyanide in the liquid under examination, which must be as concentrated as possible, is decomposed by means of a current of carbonic anhydride. Alcohol (90—95 per cent.) is added, to precipitate the potassium carbonate, and the filtrate treated with a few drops of acetic acid, and then with cobalt acetate solution. In this way, the presence of 0.0033 gram of potassium cyanate in 100 c.c. of liquid may be detected. The decomposition of 3 grams of potassium cyanide (10 per cent. solution) occupies about 45 minutes. When larger quantities have to be employed, the salt is dissolved in the smallest possible quantity of water and mixed with alcohol so as to precipitate most of the cyanide, the filtrate being then treated with carbonic anhydride as above. The presence of 1—0.35 parts of cyanate in 100 parts of cyanide is easily detected. Aqueous solutions of potassium cyanate are less stable than alcoholic, but the former do not decompose so readily as is generally stated, in one experiment 50 c.c. of potassium cyanate solution (1 per cent.) gave the cobalt reaction after being rapidly boiled for an hour; heating, even of alcoholic cyanate solutions intended for analysis, should be avoided.

J. B. T.

**Discrimination between Lactose and Glucose in Adulterated Peptones.** By L. RUZAND (*J. Pharm.*, 1895, [6], i, 232—233).—Five grams of the sample is dissolved in 45 c.c. of water and 5 c.c. of hydrochloric acid, heated for two hours in a water bath at 70°, and neutralised with aqueous soda; the liquid, which may now contain glucose and galactose, is mixed with 12 grams of sodium acetate and 8 grams of phenylhydrazine hydrochloride, and again heated for an hour. The whole is then filtered boiling; phenylglucosazone is insoluble, but the galactose compound is soluble, and crystallises out on cooling; after washing and recrystallising from hot water, it is dried, and its melting point is taken; this should be 188—191°.

A more simple test is based on the fact that neutral copper acetate is reduced by glucose, but not by lactose. If, however, the latter is

first inverted by treating with acid, as described, it also reduces the copper.

L. DE K.

### Identification and Estimation of Carbohydrates in Milk.

By ALEXANDER WYNTER BLYTH (*Analyst*, 1895, **20**, 121—126).—The paper is chiefly devoted to an improved process of recognising and estimating added sugars in milk; 25 c.c. of milk is diluted to 50 c.c. with water, and acetic acid is added drop by drop, until the casein separates. After heating to boiling, the liquid is whirled in a glass cylinder by the aid of a centrifugal machine. The bulk of the proteid and fatty matters separate, and adhere to the bottom of the cylinder, and the supernatant liquid is easily filtered. The filtrate may be examined polarimetrically, and the reducing sugars estimated by the copper cyanide process.

To identify foreign sugars with certainty, it is well to prepare the osazone; in this case, the filtrate is evaporated down to 30 c.c., and the filtered liquid mixed with 2 grams of sodium acetate, and 1.5 gram of phenylhydrazine hydrochloride. After warming for an hour and a half in a water bath, it will be found that, on cooling, the liquid becomes almost solid; the crystals are collected, pressed between blotting paper, and dried in a water oven. The osazone is then boiled with absolute alcohol (30—40 c.c.), and when dissolved allowed to stand over night; if glucose or invert sugar is present in the milk, well defined crystals will separate. The alcoholic filtrate is now heated to boiling on the water bath, water is added until a slight turbidity shows itself, and the whole is then allowed to slowly evaporate, when the osazone will crystallise out. If entirely due to lactose it looks under the microscope as aggregations of warty masses, but if partly due to glucose, bundles of needle-shaped crystals will be noticed.

L. DE K.

**Melitriose (Raffinose) and its Estimation.** By A. BAU (*Chem. Zeit.*, 1894, **18**, 1794—1799).—After a detailed historical account of the discovery and investigation of raffinose, the author describes his investigation of its behaviour towards yeast, and his experiments on its estimation. Raffinose crystallises in long, pointed needles, the specific refractive power  $[\alpha]_D = +104.0$ , and it yields an undecacetyl derivative. These properties are given incorrectly in many text-books. The experiments with yeast were all performed with pure cultures and sterilised solutions; the results show that it is quite unfermentable with bottom fermentation yeast, and only partially so with top fermentation yeast, as the melibiose which is formed undergoes no change. From experiments with *Monilia candida*, it is almost certain that raffinose is not directly fermentable. The presence of raffinose in barley has been demonstrated by the preparation of the osazone from the fermented and purified extract. Of the various methods proposed for the estimation of raffinose, the fermentation one gives, as a rule, the most satisfactory results; the solution of the substance (10—12 per cent.) is mixed, if needful, with nutritive solution, sterilised, and divided into four portions. Two of these are treated with top fermentation, two with bottom fermentation yeast,

pure cultivations being employed; the time required for fermentation is at least 10—14 days; the liquid is made up to its original weight with sterilised water, filtered, and the filtrate analysed (polarisation, cupric reducing power, and extractive matter), the difference between the extract of the two fermentations, multiplied by 1.737, gives the amount of raffinose. No correction is necessary for the yeast. Reference is made to E. Fischer and Thierfelder's experiments on the fermentability of galactose (*Abstr.*, 1894, i, 486). J. B. T.

**Estimation of Starch.** By P. L. HIBBARD (*J. Amer. Chem. Soc.*, 1895, ii, 64—68).—A weighed quantity of the sample, containing at least 0.5 gram of starch, is placed in a flask with 50 c.c. of water, and 1—2 c.c. of malt extract, prepared by soaking coarsely pulverised malt with water containing 20 per cent. of alcohol. The mixture is at once heated to boiling, shaking frequently, to prevent formation of insoluble clots. If, however, the material is poor in starch, the addition of malt is at first omitted; the liquid is boiled for a minute, and when again cooled down to 50—60°, 2—3 c.c. of malt solution is added; it is then again slowly heated to boiling, and tested for starch with iodine. When all the starch has disappeared, the mixture is cooled, made up to a definite bulk, and filtered through fine muslin; an aliquot part of the filtrate, corresponding with about 0.3 gram of starch, is then placed in a 100 c.c. flask with 5 c.c. of 30 per cent. hydrochloric acid, and sufficient water to make up to 60 c.c. This solution is now boiled gently for 30 minutes on a sand bath, then cooled, nearly neutralised with aqueous soda, and the dextrose estimated with Fehling's solution. A blank experiment is, of course, made to ascertain the amount of dextrose yielded by the malt extract.

L. DE K.

**Detection of Formalin.** By H. DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, 1895, 20, 154—156).—Guided by Pulvermacher's researches on compounds of formaldehyde with substituted ammonias, the authors have worked out the following process:—Diphenylamine is dissolved in water with the aid of sulphuric acid; the liquid to be tested (milk for instance) is distilled, the distillate added to the reagent, and boiled. In the presence of formaldehyde, a white, flocculent precipitate is deposited which occasionally may be green, due to nitric compounds in the sulphuric acid.

L. DE K.

**Estimation of Furfuraldehyde in Pentoses and Pentosans.** By B. WELBEL and S. ZEISEL (*Monatsh.*, 1895, 16, 283—311).—The authors base their method of estimating furfuraldehyde in pentoses and pentosans on the observation that in presence of a 12 per cent. solution of hydrochloric acid, phloroglucinol and furfuraldehyde condense in the cold, and even more readily on heating, forming a dark coloured, insoluble compound. This compound can be collected in a tared asbestos filter, dried at 100—110°, and weighed.

G. T. M.

**Detection of Salicylic acid in Wines.** By MATTEO SPICA (*Gazzetta*, 1895, 25, i, 207—216).—The ferric chloride test for salicylic acid, although satisfactory for the examination of beers, is of



less value in the case of wines, as the ether used in extraction takes up small quantities of tartaric, tannic, and acetic acids, together with the salicylic acid, and so masks the colour test.

The author uses a modification of Rösé's method by which the wine is extracted with ether, the ethereal solution evaporated, and the residue taken up by light petroleum, in which tartaric acid is insoluble; the ferric chloride test is then applied to the residue obtained on evaporating the petroleum solution. Should the colour obtained be faint, it is well to render the wine alkaline and concentrate before extracting; in order to prevent the repetition of the process thus involved, the residue obtained on evaporating the ethereal solution is warmed with concentrated nitric acid, rendered alkaline with ammonia, and the solution heated with a thread of white wool previously freed from grease by potash and ether. The presence of salicylic acid is betrayed by the yellow colour given to the wool by the picric acid produced; the test is not affected by the presence of tartaric, tannic, or acetic acid, and is sensitive to 0.02 milligram of salicylic acid per litre of wine if 10–25 c.c. of the latter is used.

W. J. P.

**Maumené's Test for Oils.** By H. DROOP RICHMOND (*Analyst*, 1895, **20**, 58–59).—The calorimeter used by the author consists of a small, deep beaker fitted inside a slightly larger one by means of a ring of cork; the outer beaker being placed in a tin cup padded with cotton-wool. Its heat capacity is estimated by placing 10 grams of water inside, noting the temperature, and pouring in 25 grams of hot water (of known temperature), and observing the resulting temperature.

The total heat evolved in a Maumené experiment, which the author calls the *relative molecular Maumené figure*, is calculated from the equation

$$\text{R.M.M} = R \times \frac{21.5}{x - 78.5} \times \frac{20 + h}{20} \times \frac{19.5}{K},$$

in which R is the observed rise in temperature from 25 grams of oil and 5 c.c. of sulphuric acid,  $x$  its percentage of real sulphuric acid (which must not be below 92°),  $h$  the heat capacity of the calorimeter in grams of water, and K the potash absorbing figure of the sample, 19.5° being taken as the average.

L. DE K.

**New Thermal Method for Examining Oils.** By OTTO HEHNER and CHARLES A. MITCHELL (*Analyst*, 1895, **20**, 146–150).—The authors prefer using bromine instead of sulphuric acid when testing oils for rise in temperature.

One gram of the oil is dissolved in 10 c.c. of chloroform and introduced into a vacuum-jacketed test-tube. A delicate thermometer is put in, and, after noticing the temperature, 1 c.c. of bromine is added, and the increase in temperature observed. The authors have tabulated the results of 31 samples of oil and fat. In nearly every case the iodine absorption figure agreed very well with the rise in temperature, and could be calculated by multiplying the latter by 5.5.

L. DE K.

**Gravimetric Estimation of Bromine Absorption of Fats.** By OTTO HEHNER (*Analyst*, 1895, 20, 49—52).—The author has found that the compounds of fats with bromine may be dried at 125° without loss, and has based on this fact a gravimetric process for determining the bromine absorption of fats.

From 1—3 grams of the sample is introduced into a small wide-mouthed flask and carefully weighed. The fat is dissolved in a few c.c. of chloroform, and bromine is then added until it is decidedly in excess. The flask is heated on the water bath until most of the bromine is driven off, a little more chloroform is added, and the mixture again heated, the chloroform vapour expelling the excess of bromine. The residue is then dried at 125° until the weight is constant.

L. DE K.

**Hübl's Iodine Absorption Method.** By JULIUS EPHRAIM (*Zeit. angew. Chem.*, 1895, 254—259).—The author has investigated the nature of the Hübl's solution (iodine and mercuric chloride dissolved in alcohol), and thinks that, as its action is chiefly due to chloride of iodine, it is more convenient to make an alcoholic solution of iodine monochloride instead. This should contain 16.25 grams of the compound per litre.

L. DE K.

**The Amorphous Nitrogenous Organic Compounds in Beer Wort.** By N. C. HENRIK SCHJERNING (*Zeit. anal. Chem.*, 1895, 34, 135—147).—It is first shown that one of the statements in the earlier paper (*Abstr.*, 1894, ii, 371) requires correction. The stannous chloride precipitate is not identical with the absolute baryta precipitate (abs. Ba), but with the absolute lead precipitate (abs. Pb = Pb — abs. Ba): the absolute baryta precipitate is therefore the same as Pb — Sn, and is best estimated by subtracting the amount of the stannous chloride precipitate from the amount of the lead acetate precipitate.

The author then proceeds to determine the amount of nitrogen extracted from malt by one hour's mashing at different temperatures, ranging from 25° to 100°, and the proportion of the nitrogen precipitated by each of his four reagents (Ba — or rather Pb — Sn, Sn, Fe, and Ur, *loc. cit.*), from each of the worts thus obtained; the greatest solubility for the nitrogenous constituents of malt, as well as the highest degree of peptonising is found at about 60°. The amount of ammonia extracted is the same at all temperatures, and is not altered by subsequent boiling of the wort for three hours. The general results seem to support Mulder's hypothesis of the derivation of the amorphous nitrogenous organic compounds in wort from a single highly complex proteid. The curves representing the changes in the amounts of the different precipitates as the temperature of mashing is varied indicate that the peptones are formed at the expense of the albuminous substances, and the propeptone chiefly at the expense of the material which the author has provisionally called "denuclein."

M. J. S.

## General and Physical Chemistry.

**Emission of Light during Crystallisation.** By ERNST BANDROWSKI (*Zeit. physikal. Chem.*, 1895, 17, 234—244).—The author, who has repeated Rose's experiments with arsenious anhydride and potassium sulphate, contests his conclusion, that the emission of light during crystallisation is due to the change from an amorphous to a crystalline state. He finds that both the crystalline and amorphous varieties of arsenious oxide emit light during crystallisation, and that these phenomena can be reproduced as often as desired by redissolving and cooling. He considers that the effect is probably due to the formation and decomposition of an arsenious salt,  $\text{As}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 3\text{H}_2\text{O}$ , and in support of this he has noticed that a hot solution of the trichloride on cooling slowly deposits the anhydride with strong development of light. The experiments with potassium sulphate are in many cases contradictory to those of Rose, and the author finds that in all cases where light is emitted the composition of the crystals corresponds with the formula  $2\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ , so that the effect is probably chemical, and connected with the formation of this double salt. In all the cases, the character of the light effects are quite different from those previously described (this vol., p. 6).

L. M. J.

**Molecular and Atomic Refraction.** By W. F. EDWARDS (*Amer. Chem. J.*, 1895, 17, 473—506).—The author has lately (this vol., ii, 193) proposed a new form of molecular "refraction equivalent,"  $P(\mu - 1)/D\mu$ , in place of the well-known ones of Gladstone,  $P(\mu - 1)/D$ , and Lorentz and Lorenz,  $P(\mu^2 - 1)/D(\mu^2 + 2)$ ; where  $\mu$  = index of refraction,  $D$  = density,  $P$  = molecular weight. He has now calculated, from the original data, the values of these three

	Gladstone. $\frac{P(\mu-1)}{D}$	Lorentz-Lorenz. $\frac{P(\mu^2-1)}{D(\mu^2+2)}$	Edwards. $\frac{P(\mu-1)}{D\mu}$
Hydrocarbons, aliphatic..	7·74	4·56	5·25
" aromatic..	8·00	4·75	4·44
Alcohols, aliphatic .....	7·68	4·62	5·28
" aromatic.....	7·48	4·45	5·14
Aldehydes, aliphatic ....	7·69	4·58	5·24
Acids, " .....	7·65	4·61	5·31
Ethereal salts, " .....	7·68	4·62	5·34
Chlorides, " .....	7·87	4·65	5·39
Bromides, " .....	7·89	4·60	5·39
Iodides, " .....	7·94	4·69	5·37
Amines, " .....	8·15	4·69	5·50
" aromatic .....	7·72	4·58	5·27
Nitriles, aliphatic .....	7·85	4·68	5·36

refraction equivalents, for sodium light, in the case of a number of liquids; and he finds that if, in different classes of organic substances, these values are used to determine the value of  $\text{CH}_2$ , variations in the mean numbers thus obtained for  $\text{CH}_2$  in the different classes are distinctly less when his form of the refraction equivalent is used than with the two others; this is shown by the preceding table, which gives these values of  $\text{CH}_2$ .

The values of the atomic refractions were then calculated in the usual way, and are given in the table below; they are the means of the numbers regarded as most trustworthy. It is not clear whether the presence of an "isolated" carbon atom, as in methylic alcohol, &c., does or does not raise the molecular refraction equivalent above the normal value. A double linking certainly does, and apparently by different amounts in the aliphatic and aromatic series; the individual numbers differed so widely in the first case, however, that the mean of those obtained in the aromatic series was regarded as the true value of a double linking of carbon atoms. Oxygen has, as usual, two values, as "hydroxyl-oxygen" ( $-\text{O}\cdot\text{H}$ ) and as "carbonyl-oxygen" ( $>\text{C}:\text{O}$ ); but if the new refraction equivalent is used, it is found to have yet a third value, namely, when it exists as "ether-oxygen" ( $>\text{C}\cdot\text{O}\cdot\text{C}<$ ); this third value was not calculated from the ethers themselves, data as to which are not considered in this paper, but from the ethereal salts of the fatty acids. Sulphur has also two values, as "thiohydroxyl-sulphur" ( $-\text{S}-$ ) in aliphatic hydrosulphides and sulphides, and as "thiocarbonyl-sulphur" ( $>\text{C}:\text{S}$ ) in xanthates and thiocarbonates. Nitrogen has different values according as it exists in primary amines ( $-\text{NH}_2$ ), in secondary amines ( $>\text{NH}$ ), in tertiary amines, pyridine, &c. ( $>\text{N}$ ), or in cyanides ( $-\text{C}:\text{N}$ ).

	$\frac{P(\mu-1)}{D}$	$\frac{P(\mu^2-1)}{D(\mu^2+2)}$	$\frac{P(\mu-1)}{D\mu}$
Carbon .....	4.68	2.45	2.01
Double bond .....	2.88	1.81	2.66
Hydrogen .....	1.50	1.08	1.64
Oxygen, hydroxyl .....	2.70	1.46	1.59
"    ethereal .....	2.73	1.53	2.13
"    carbonyl ..	3.25	2.35	3.38
Sulphur, thiohydroxyl ...	13.47	7.66	8.36
"    thiocarbonyl ...	19.76	11.02	11.85
Nitrogen, primary .....	5.01	2.49	1.99
"    secondary .....	5.09	2.71	2.35
"    tertiary .....	5.54	3.26	3.13
"    in cyanides ....	4.63	3.20	4.79
Chlorine .....	10.11	6.03	7.20
Bromine .....	15.32	8.84	9.95
Iodine .....	25.09	14.01	15.22

C. F. B.

**Spectra of Gases evolved from various Minerals.** By J. NORMAN LOCKYER (*Compt. rend.*, 1895, 120, 1103—1104).—The author

has heated 18 minerals, including uraninite, in a vacuum, and examined the spectra of the gases given off. The various spectra contain altogether about 60 lines which do not coincide with lines of any known terrestrial bodies. Seventeen lines have been photographed, and their wave-lengths (on Rowland's basis) are as follows.

3889 (1, 2, 3)	4177 (2, 3)	4453 (2).
3947 (1, 2)	4182	4471 (1, 2, 3).
3982 (2)	4338 (1, 3)	4515 (1, 2).
4026.5 (2, 3)	4347 (3)	4522 (1, 2).
4142	4390 (1, 2, 3)	4580
4145 (2, 3)	4398 (1, 2)	—

Those marked (1) seem to be identical with lines of unknown origin observed in the sun's chromosphere, those marked (2) with lines photographed during the eclipse of 1893, and those marked (3) with lines in the white stars of Orion.

C. H. B.

### Spectra of Gases from Cleveite, and the Solar Spectrum.

By HENRI DESLANDRES (*Compt. rend.*, 1895, **120**, 1112—1114).—The gas from Cleveite, (1) in a vacuum at the ordinary temperature, (2), in a vacuum at 300°, and (3), after heating with sulphuric acid in a vacuum, was examined separately. The gas given off at the ordinary temperature showed some of the lines of argon; that given off at 300° contained a considerable quantity of an oxygen compound of carbon, whilst that evolved on treatment with acid showed the line D<sub>3</sub> and many other strong lines, the wave-lengths and intensities of which are as follows.

λ.	Intensity.	λ.	Intensity.	λ.	Intensity.
*6678.0	5	*4437.9	4	3819.7	5
*5876.0	10	*4388.4	6	*3705.4	4
*5048.4	4	4143.9	5	3613.8	5
*5016.0	9	4120.9	5	3447.7	4
*4922.2	6	4026.2	8	*3187.9	7
*4713.35	7	*3964.0	7	2945.7	5
*4471.75	8	*3888.75	10	—	—

The first six were observed by Cleve, and those marked \* have been observed in the sun's chromosphere. With the exception of D<sub>3</sub>, the author did not observe the lines described by Crookes.

The gas from Cleveite shows, in addition to the line D<sub>3</sub>, several strong lines observed in the chromosphere, and notably the line 4471.8, which is always present in the chromosphere. It follows that the number of lines constantly observed in the sun and not corresponding with lines shown by terrestrial substances is reduced to two.

Some of the lines from Cleveite do not show the same relative intensity as compared with D<sub>3</sub> as in the solar spectrum. It would seem, therefore that the gas is a mixture or a compound, and this is supported by the fact that in the spectrum tube D<sub>3</sub> is only seen at the positive pole and in the capillary portion, whilst the line 501 is very brilliant at the negative pole.

C. H. B.

**Variations observed in the Spectra of Carbon Electrodes.** By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1894, **55**, 344—349).—This paper contains a reply to Eder and Valenta's criticisms (*Akad. Wiss. Denksch. Wien.*, 1893, **60**) on a previous paper by Hartley and Adeney. The author still thinks that the lines with the wave-lengths 3881·9, 3870·7, 3589·9, 3584·8, are carbon lines, and not the edges of cyanogen bands, as Eder and Valenta state. These same lines are obtained from the combustion of cyanogen and from carbon electrodes surrounded by saline solutions, but are not given by cyanides. A list is given of the lines which appear under different circumstances when condensed sparks are passed between graphite electrodes. This list includes the lines of dry electrodes in air, in carbonic anhydride, and in oxygen. J. J. S.

**Flame Spectra at High Temperatures. Part II. Spectrum of Metallic Manganese, of Alloys of Manganese, and of Compounds containing that Element.** By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1894, **56**, 192—193).—Photographs of the spectra of metallic manganese and of manganic oxide were taken and compared. They were also compared with the spectra of the alloys of manganese. The periods of exposure varied from a mere flash in the case of Spiegeleisen when poured into a Bessemer converter, to 30 minutes, and even as much as 80 minutes with manganic oxide. The leading features of the spectra of manganese and manganese oxide are the same, but they differ in detail, as may be observed by comparing the wave-lengths of the lines and bands in their respective spectra. A striking group of lines, the most persistent in the whole of these spectra, is situated in the violet. The following measurements were made:—4036·5, 4032·0, 4029·5. Another line is just visible about 4031·8, but it is so close to 4032·0 that it could be discerned only when the extreme points of three very strong lines were examined and the plate was in perfect focus for that region. E. C. R.

**Flame Spectra at High Temperatures. Part III. The Spectroscopic Phenomena and Thermo-Chemistry of the Bessemer Process.** By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1894, **56**, 193—199).—The constitution of the Bessemer spectrum is a complex one, which exhibits differences in constitution during different periods of the "blow" and even during different intervals in the same period. As originally observed by Watts, the spectrum differs at different works, the difference being due to temperature and to the composition of the metal blown. During the first period, the lines of the alkali metals, sodium, potassium, and lithium are seen unreversed on a bright continuous spectrum caused by carbon monoxide. The C line of hydrogen and, apparently, the F line, were seen reversed during a snowstorm. During the second period, the "boil," bands of manganese are prominent, overlying the continuous spectrum of carbon monoxide. There are lines of carbon monoxide, manganese, and iron, also those of the alkali metals. During the third period, the "fining stage," the spectrum is the same as the foregoing, but the lines of iron are not so strong and not quite so well defined. Some of the short lines dis-

appear. The lines of the alkali metals are visible. No absorption bands were seen, no nitrogen bands, nor bands of calcium, or magnesium oxide, neither did the lines of these metals appear. There is no trace of cobalt, nickel, chromium, or copper. Some of the lines not identified by Watts prove to be iron lines, others belong to manganese.

The non-appearance of the lines of manganese at the commencement and termination of the blow is owing to the quantity of metal volatilised at these periods being insufficient for the production of a spectrum. At the commencement, the temperature is too low. The alkalis come from the ganister lining of the converter, and do not show themselves until a layer of slag has been formed and the temperature has risen sufficiently high for their basic constituents to be vaporised. At the temperature of the "boil," metallic manganese and iron are freely vaporised in a current of carbon monoxide, which, in a highly heated state, rushes out of the bath of molten metal. When the metal blown contains but little manganese, this is all converted into silicate during the first period. The manganese spectrum of the flame does not arise from that substance being contained in the bath of metal, it must be vaporised from the slag. This has been proved by photographs of the spectrum from samples of slag obtained from the Crewe works. The luminosity of the flame during the "boil" is due not merely to the combustion of highly heated carbonic oxide, but also to the presence of the vapours of iron and manganese in the gas. The disappearance of the manganese spectrum at the end of the "fining stage" is primarily due to a reduction in the quantity of heated carbon monoxide, and also, when the last traces of carbon are gone, to the oxidation of the manganese by the blast. The probable temperature of the Bessemer flame at the finish is that produced by the combustion in cold air of carbonic oxide heated to about 1580°. Judging by the lines and bands of iron and manganese which have been measured in photographed spectra of the Bessemer flame, the temperature must nearly approach 1775°. From thermochemical data, the heat evolved during the "blow" has been calculated. If we allow for 50 per cent. of the heat developed at high temperatures being lost by radiation or absorbed, then the estimated temperature of the metal in the converter is more than 1900°. E. C. R.

**Absorption Spectra of Dilute Solutions.** By THOMAS EWAN (*Proc. Roy. Soc.*, 1894, 56, 286—287).—The absorption spectra of solutions of cupric sulphate, chloride, bromide, and nitrate, containing 0.003 to 0.004 gram mol. per litre were found to be, within the limits of experimental error, identical. Solutions of cupric acetate absorb, for the same amount of copper, much more light than those of the other salts used. The difference tends to disappear as the solutions become more dilute, and it is increased by the addition of acetic acid. The difference is due to the incomplete electrolytic dissociation of the salt, and to the undissociated part having an absorption spectrum differing from that of the dissociated part. Dilute solutions of the potassium and ammonium derivatives of  $\alpha$ -dinitrophenol [1:2:4] were found to have very nearly the same absorption spectrum.

The mean of the numbers obtained was regarded as the absorption spectrum of the ion  $C_6H_3(NO_2)_2O$ . The solution of dinitrophenol in hydrochloric acid absorbs very little light; it is almost colourless. The extinction coefficients of dinitrophenol and of its coloured ion, being thus known, it was possible to calculate from measurements of the extinction coefficients of a series of solutions of dinitrophenol in pure water, its degree of dissociation in these solutions. The numbers obtained agreed satisfactorily with the numbers calculated from the electrical conductivity of the solutions.

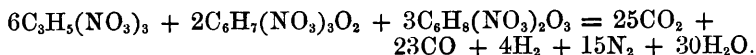
By filtering dilute solutions of ferric chloride through a porous cell all the colloidal ferric hydroxide formed can be removed; and the analysis of the solutions before and after filtration showed that the hydroxide formed in solutions containing less than 0.005 gram mol. of  $FeCl_3$  per litre, contains no chlorine. The photometric determinations of the quantity of ferric hydroxide formed in these solutions agreed fairly well with the results of the filtration experiments. The quantities of ferric hydroxide found are not in agreement with the law of Guldberg and Waage, but agreed much better with Arrhenius' modified law. Solutions of ferric hydroxide obtained by dissolving ferric chloride in a very large quantity of water, had a different absorption spectrum from that of solutions of ferric hydroxide obtained by dialysis. Solutions of ferric chloride, to which small quantities of hydrochloric acid have been added, possess such comparatively small power of absorbing light that they cannot be regarded as containing any colloidal ferric hydroxide.

E. C. R.

**Researches on Modern Explosives.** By WILLIAM MACNAB and E. RISTORI (*Proc. Roy. Soc.*, 1894, **56**, 8—19).—The explosives used in these experiments can be divided into three classes. (1.) Those consisting of nitrolignin or nitrocellulose (not gelatinised), mixed or impregnated with a suitable nitrate, and mixed with colouring matters and some other substances, for the purpose of retarding the rate of combustion. (2.) Those containing purified nitrolignin or nitrocellulose gelatinised by a suitable process, and with or without the addition of nitrobenzene or other suitable nitrates. (3.) Those containing nitrocellulose combined with nitroglycerin, with the addition of aniline, camphor, vaseline, or other kindred substances. Also a series of samples of ballistite were specially made, containing nitroglycerin and nitrocellulose in various proportions. Using a bomb of 247.6 c.c. capacity, with a density of loading of  $\Delta = 0.1$ , i.e., with a charge of 24.76 grams, the average of the pressures measured was 6.3 tons per square inch; with density  $\Delta = 0.2$  the pressure rose to 15 tons, and with  $\Delta = 0.3$  the pressure increased to 25 tons. The amount of heat generated by the explosion, the volume and composition of the permanent gases produced, and the quantity of aqueous vapour formed, were ascertained. The average weight of the products of explosion, calculated from the results found, amounts to 99.7 per cent. of the weight of the explosive fired. The use of highly nitrated cellulose increases the quantity of heat developed, and diminishes the volume of gas; the composition of the permanent gases is also altered, there being an increase in carbonic



anhydride and a decrease in carbonic oxide and hydrogen. When a smaller proportion of explosive in comparison with the air is present, the combustion is more complete, and the heat developed is greater. The reaction which takes place with an explosive containing 50 per cent. of nitroglycerin and 50 per cent. of nitrocellulose may be expressed by the following equation :



Complete tables of the results are given in the paper. E. C. R.

**Heats of Solution and Dissociation.** By MAX RUDOLPHI (*Zeit. physikal. Chem.*, 1895, **17**, 277—300).—Owing to the difficulty of directly determining the heat of solution of sparingly soluble salts, the author investigates thermodynamically an expression for this value. The expression  $W = -1.98 T^2/C_1 \cdot dC/dT$  is obtained if no dissociation occurs, C being the molecular concentration and W the molecular heat of solution. The correction to be applied, owing to dissociation, is next determined, the expression  $-Q/T^2 = (1/C + 2/C_2) \cdot dC_2/dT$  being obtained where  $C_1$  and  $C_2$  are the concentrations of undissociated salt and ion respectively. The salts examined were the acetate, propionate, butyrate, isobutyrate, and isovalerate of silver, the necessary solubility values being taken from the determinations of Raupenstrauch and Sedlitzky. The dissociation values were obtained by determinations of the conductivity by Kohlrausch's method, the conductivity of the corresponding sodium salts, and of the nitrates of sodium and silver, supplying the values at infinite dilution. The values for the heat of solution of saturated solutions are thus obtained ( $L = Q \lambda_v/\lambda_\infty + W$ ), and recorded in the accompanying table.

	Acetate.	Propionate.	Butyrate.	Isobutyrate.	Isovalerate.
25° ..	-3.120	-4.103	-3.005	-2.357	-3.205
30 ..	-3.366	-3.433	-2.954	-2.051	—
35 ..	-3.150	-3.112	-4.200	-2.019	-4.181
					L. M. J.

**Isomeric Changes of Mercury Compounds.** By RAOUL VARET (*Compt. rend.*, 1895, **120**, 1114—1115).—Determinations of the thermal disturbances accompanying the dissolution of the various forms of mercuric sulphide in a saturated solution of sodium sulphide in sodium hydroxide solution of sp. gr. 1.4, lead to the following results.

HgS black amorphous	= HgS red amorphous	develops	+0.24 Cal.
HgS „ „	= HgS red crystallised	„	+0.30 „
HgS red amorphous	= HgS red crystallised	„	+0.06 „
			C. H. B.

**Thermochemical Relations between Aldehydes, Alcohols, and Acids.** By MARCELLIN BERTHELOT and PAUL RIVALS (*Compt. rend.*, 1895, **120**, 1086—1095).—Determinations by means of the calorimetric bomb gave the following results.

	Heat of combustion (constant pressure).	Heat of formation (carbon as diamond).
Saligenol .....	846.0 Cal.	+ 90.1 Cal.
Salicylaldehyde .....	807.6 "	+ 59.5 "
Pyromucic acid .....	493.8 "	+ 115.7 "
Furfuraldehyde .....	559.8 "	+ 49.7 "
Campholenic acid, solid..	1365.9 "	+ 129.1 "
" " liquid.	1363.3 "	+ 131.7 "
Campholic acid .....	1409.2 "	+ 154.8 "

Saligenol is both an alcohol and a phenol, and its heat of formation is +21.3 Cal. less than that of the isomeric dihydric phenol, orcinol. A similar difference, +15 Cal., is observed between benzylic alcohol and ortho- and para-cresol, and in all cases the conversion of an alcoholic function into a phenolic function is accompanied by a considerable development of heat, correlated with the increased general stability and the increased activity of the acidic function. The differences in question do not correspond with any relation between phenols and tertiary alcohols.

Comparison between the values for salicylaldehyde and benzoic acid shows that the change from aldehyde-phenol function to acid function develops +34.7 Cal., which is greater than the thermal disturbance usually accompanying the change from alcohol-phenol to diphenol. The oxidation of saligenol to salicylic acid develops +111.0 Cal., and the oxidation of salicylaldehyde to acid +72.6 Cal., whilst the direct hydrogenation of salicylaldehyde with formation of saligenol develops +30.6 Cal.

Comparison of the heat of formation of pyromucic acid with that of mucic acid, +426.9 Cal., shows that the difference, +301.3 Cal., corresponds exactly with the heat of formation of  $\text{CO}_2 + 3\text{H}_2\text{O}$ , which agrees with the relation established in the case of other pyrogenic acids.

Furfuraldehyde contains hydrogen and oxygen in the same proportions as in water, and if the heat of formation of the aldehyde is subtracted from that of the water, the difference, +88.3 Cal., is the excess of energy possessed by a molecule of furfuraldehyde, regarded as a hydrate of carbon, or, in other words, the excess of its heat of combustion over the heat of combustion of the carbon which it contains. Glucose, when regarded in the same way, has an excess of energy of +91.4 Cal.; pyrogallol, which has a very different function, an excess of +77.5 Cal., acetic acid an excess of +18.3 Cal. for  $\text{C}_2$  or +54.9 Cal. for  $3\text{C}_2$ . It follows, that compounds which may be regarded as hydrates of carbon, although having very various functions, retain, as a rule, an excess of energy, a fact which it is essential to keep in mind in all investigations concerning animal heat, or in estimating the heating power of combustibles. The excess calculated for the same number of carbon atoms is highest in the case of alcohols and aldehydes, less in the case of phenols, and still less in the case of acids, each of these changes of function being accompanied by a special development of heat, even in the case of isomerides.

In the case of arabinose, which readily splits up into furfuraldehyde and water, the excess is  $+17.1 \times 5$  or +85.6 Cal., and is of the same order of magnitude as in the case of glucose. The conversion of

arabinose into furfuraldehyde corresponds with a thermal disturbance of only  $-2.2$  Cal.

The product formed by the spontaneous condensation of furfuraldehyde has the composition  $C_{15}H_{10}O_5$  or  $3C_5H_4O_2 - H_2O$ , and its heat of combustion is  $1684.2$  Cal., and its heat of formation  $+75.3$  Cal. It follows that its formation from furfuraldehyde, with elimination of water, absorbs only  $-4.8$  Cal.

The heat of dissolution of furfuraldehyde is  $+0.13$  Cal. at  $6^\circ$ , and potassium hydroxide produces no thermal disturbance when added to the solution.

In the camphenic series, it follows, from previous determinations of the heats of formation, that the oxidation of borneol to camphor, with elimination of water, develops  $+52.0$  Cal., and the direct hydrogenation of camphor develops  $+17.0$  Cal.

The difference between the isomeric campholenic acids, assuming that the latent heat of fusion of the solid acid is about  $-4$  Cal., is only  $6$  Cal., and is of the same order and magnitude as the difference between fumaric and maleic acids (compare Béhal, this vol., i, 553). Adopting the value for the solid acid, it would follow that the oxidation of camphor to campholenic acid develops  $+48.8$  Cal., and the oxidation of borneol, with simultaneous formation of water,  $+100.8$  Cal. The oxidation of camphor to camphoric acid develops  $+170.9$  Cal. or  $+57.0 \times 3$ .

The hydration of camphor with formation of campholic acid develops  $+5.5$  Cal. if the water is liquid, and  $+4.1$  Cal. if the water is solid, the thermal disturbance being of the same order as in the conversion of glyoxal into glycollic acid.

Comparison of all the thermal measurements that bear on the relations between alcohols, phenols, aldehydes, and acids, leads to the general conclusion that the conversion of a true aldehyde into an alcohol by addition of  $H_2$  develops from  $+13$  to  $+17$  Cal., the mean being about  $15$  Cal. in the paraffin series, whether the alcohol is mon-hydric or polyhydric.

From this point of view, camphor belongs to the paraffin series, a conclusion also deducible from the well-known synthesis of the hydrocarbons  $C_{10}H_{18}$  from the hydrocarbons  $C_5H_8$ .

In the benzene series, the corresponding thermal disturbance is much higher, the fixation of  $H_2$  developing  $+40$  Cal. in the case of quinone, and  $+30$  Cal. in the case of salicylaldehyde.

The conversion of an aldehyde into an acid by combination with  $O$ , develops from  $60$  to  $68$  Cal., except in the case of camphor, which belongs to a special group, and develops only  $+48.8$  Cal., a result which supports Béhal's views (*loc. cit.*). Camphor, in fact, resembles glyoxal, the oxidation of which to glyoxylic acid develops  $+45.6$ , whilst the latter, when oxidised to oxalic acid, develops the normal  $+66.8$  Cal. On the other hand, salicylaldehyde when oxidised develops  $+72.6$  Cal., which is higher than in the case of any other aldehyde.

The conversion of an alcohol into an aldehyde as a rule develops less heat than the oxidation of an aldehyde to an acid. All the combinations with oxygen develop less heat than the oxidation of free hydrogen; but the difference would be much smaller if the heat of

liquefaction of hydrogen were known, and the calculations could be referred to the same physical state. On the other hand, the combination of aldehydes with hydrogen in the paraffin series develops much less heat than the formation of water, and hence the alcohols retain a reserve of available energy which comes into play in their subsequent oxidations.

C. H. B.

**Cryosalts.** By A. PONSOT (*Bull. Soc. Chim.*, 1895, [3], **13**, 312—316).—If the strength of a solution of an ordinary crystallisable salt is plotted against the temperature in the usual manner, the points representing its possible values fall between, and to the right of, two intersecting inclined lines, one of which rises with the temperature and represents the maximum concentrations, or states of saturation at the various temperatures, and the other which falls as the temperature rises, and represents the minimum concentrations. Points above the first line thus represent unstable states in which the solution is supersaturated with the salt, whilst those below the second line represent unstable states in which the solution is supersaturated with ice. The point of intersection, and points between the lines to the left of this, therefore represent states in which crystals either of the salt or of ice may separate from solutions of the requisite strength on cooling to the requisite temperature.

The author has verified this last deduction by microscopic examination of the crystalline products obtained by freezing solutions of coloured salts, such as potassium permanganate and dichromate, and of colourless salts affecting polarised light, such as potassium chloride and nitrate. In every case, the so-called cryohydrate was found to be a mixture of microscopic crystals of the salt and of ice, and the salts thus separated were either anhydrous, or combined with comparatively small, and molecularly simple, amounts of water.

The separation of the ice may be effected on a larger scale by freezing the solution in a test-tube, and then melting the middle part of the mass. When the liquid zone has reached nearly to the bottom, the tube is again exposed to a low temperature and shaken continuously, with the result of increasing the proportion of ice in the mass of crystals floating at the top, and by repeating the operation a sufficient number of times, ice may be obtained in any desired degree of purity.

Guthrie's cryohydrates cannot therefore be regarded as chemical individuals, and Pfaundler's views as to their nature are confirmed. The author proposes to substitute the term *cryosalt* (*cryosel*) for the older term cryohydrate, and suggests that the temperatures of formation of such salts be used as characteristic constants. JN. W.

**Cryohydrates.** By MAX ROLOFF (*Zeit. physikal. Chem.*, 1895, **17**, 325—356).—The paper contains the determinations of the composition of a number of cryohydrates of various pairs of compounds, by means of the measurement of the lowering of the freezing point of each component by varying quantities of the other, and hence obtaining the cryohydrate composition from the point of intersection of the curves, usually straight lines. The following results were so ob-

tained :—Benzoic acid and benzene, composition 5.1 per cent. benzoic acid, freezing point  $-4.2^{\circ}$ ; acetic acid and benzene, 36.1 per cent. acetic acid,  $-8.8^{\circ}$ ; naphthalene and diphenylamine, 30.1 per cent. naphthalene,  $32.45^{\circ}$ . In the case of a mixture of naphthalene with thymol, satisfactory results were not obtained. The effect of external pressure on the composition of the cryohydrate is next considered, and the value  $dp/dT$  deduced theoretically. It is also determined experimentally by the use of the mano-cryometer (Abstr., 1893, ii, 563). The same coefficient is also obtained by making use of Thompson's formula,  $dT/dp = T/J \times (\sigma - T)10333/w$ , where  $\sigma - T$  is the volume increment on melting (c.c. per kilo.), and  $w$  the heat of liquefaction, these constants being experimentally determined. The values obtained in the case of the mixture of naphthalene with diphenylamine were respectively 34.1, 33.2, and 32.1 atmospheres per degree centigrade. The effect of a third component is next investigated, the first experiments being on acetic acid and benzene with the addition of water. The cryohydrate minimum is thus lowered, and occurs at a higher acetic acid content than the normal, the more so the greater the water content. With vaseline—soluble in benzene, insoluble in acetic acid—the minimum is again lowered, but corresponds with a higher benzene content, the effect of naphthalene being very similar.

L. M. J.

**Molecular Weight Determinations in Solid Solutions.** By FRITZ W. KÜSTER (*Zeit. physikal. Chem.*, 1895, 17, 357—373).—In order to determine the molecular weight of a compound present in a solid solution, the author considers the equilibrium of  $\beta$ -naphthol, naphthalene, and water, in which case the two solids are non-electrolytes, the one being soluble, the other insoluble in water, and he shows experimentally that they are capable of forming a homogeneous, isomorphous mixture, a result at variance with those obtained by van Bijlerts (Abstr., 1891, 1411). The solubility of the  $\beta$ -naphthol for decreasing naphthalene content rises regularly to a maximum, when it suddenly falls to a constant value equal to the solubility of the pure naphthol. The ratio of the partition coefficients in water and naphthalene is not constant, but an approximately constant value is obtained for the ratio  $\sqrt{K_s}/K_w$ , where  $K_s$  and  $K_w$  are the concentrations of the naphthol in the solid and aqueous solutions. The molecule of the naphthol in the solid solution is hence double of what it is in the aqueous solution, that is,  $2C_{10}H_8O$ , the naphthalene being  $2C_{10}H_8$ . The complexity of the crystals of the isomorphous mixture is determined by the alteration of the solubility of the naphthol and naphtholnaphthalene. The best results for the maximum solubility are obtained on the supposition that the mixture has the complexity  $x C_{10}H_8, (2-x) C_{10}H_8O$ , which yields the values for the solubility 0.0775 and 0.0675 at  $18^{\circ}$  and  $25.1^{\circ}$ , the observed values being 0.0780 and 0.0682. The complexity of the molecules in the solid solution are hence respectively  $2C_{10}H_8, 2C_{10}H_8O$ , and  $(C_{10}H_8, C_{10}H_8O)$ .

L. M. J.

**History of the Periodic System.** By KARL SEUBERT (*Zeit. anorg. Chem.*, 1895, 9, 334—338).—Lothar Meyer gave A. Remele,

his successor at Eberswalde, in July, 1868, a paper containing a periodic arrangement of the elements; it is headed "§ 91," and evidently intended for a new edition of his '*Modernen Theorien.*' It contains 52 elements, arranged in 15 vertical series (families), instead of the 28 elements in six series given in the first edition. In Mendeléeff's first table, published in 1869, the elements in each period are arranged in vertical columns. J. B. T.

**Classification of Chemical Elements.** By PAUL E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, **120**, 1097—1103) and by CHARLES FRIEDEL (*ibid.*, 1103).—In calculating the atomic weights of a hypothetical family of elements, which may form an eighth column in Mendeléeff's table (this vol., ii, 257), the author considered only the elements with atomic weights above 20, and regarded the elements which usually appear in the eighth column as not belonging to the same family at all. The classification, however, indicates the possible existence of an element below the element 20.1, with an atomic weight of about 3.9, and an element in the chlorine family below fluorine, with an atomic weight of about 2.9.

Ramsay's determination of the sp. gr. of helium gives 3.88, and hence the specific gravities of argon and helium respectively agree with the numbers which the author predicted as the atomic weights of hypothetical elements, with which they seem to correspond.

In each well-established natural family of elements, there is one which seems to possess in a special degree the properties characteristic of the family, and of which it may be regarded as forming the centre or *node*. These elements are Ca, K, ( $\delta$ ), Cl, S, P, Si, Al, and if they are placed in line, the line is the higher limit of the atomic weights which increase by increments of about 16, and the lower limit of the atomic weights which increase by larger increments, such as 48. The higher groups of three attached to these elements (e.g., Ca, Sr, Ba, or Cl, Br, I) are all comparable amongst themselves from both a chemical and a spectroscopic point of view, and their variations, or, in other words, the differences between the first increase of about 48 and the second, are comprised within very narrow limits. If any other elements are taken as the nodes, these relations do not hold good. With the arrangement proposed by the author, the atomic weight of one node can be calculated from the atomic weights of the others, and comparison of the variations enabled the author to calculate accurately the atomic weights of gallium and germanium. The table on this basis is—

				(? $\eta$ )''	Bi'	Pb''	Tl'	
	Ba''	Cs'	(? $\zeta$ )''	I'	Te''	Sb'	Sn''	ln'
	Sr''	Rb'	(? $\epsilon$ )''	Br'	Se''	As'	Ge''	Ga'
Nodes	Ca''	K'	(? $\delta$ )''	Cl'	S''	P'	Si''	Al'
	Mg''	Na'	(? $\gamma$ )''	F'	O''	N'	C''	B'
	Be''	Li'	(? $\beta$ )''	(? $\alpha$ )'				
	H	H	H	H	H	H	H	H

All the groups contain the same number of elements. Where the atomic weight of the node is more than 32, there are two elements

between it and hydrogen, but where it is less than 32 there is only one element between the node and hydrogen. In the latter cases, however, there is an additional element above the higher group of three [( $\eta$ ), Bi, Pb, Tl]. Starting from hydrogen, each family is formed by five successive increments, and it would seem that hydrogen itself has been formed by addition to some element of still lower atomic weight, or that hydrogen and the seven other elements of small atomic weight on the same line have been formed by addition to eight others on a still lower line.

In the table, elements of odd and even quantivalence alternate. The electro-negative elements are in the middle, and the relatively strongly electro-positive elements are at the extremities. In the case of both metals and non-metals, that element of each pair which has the lower atomic weight has odd quantivalence.

If it is supposed that a mass of primordial matter A is, by some cause, divided into two unequal parts, two elements belonging to the same horizon will be produced,  $A/2 + q$  and  $A/2 - q$ , the one being electro-positive with respect to the other. A repetition of the process will result in four elements, two electro-positive and two electro-negative, and so on. If it is assumed that eight elements are formed in this way, they might give rise by successive additions, or subtractions, to the eight families included in the table, and the additions or subtractions would correspond with variations in properties in both a horizontal and a vertical direction. It is obvious that, on this hypothesis, there must be an even number of families. From this point of view, the formation of chemical elements depends on inequalities between masses of matter, just as forces result from inequalities in the motions of bodies, and in both cases there is compensation between the masses (or movements) of opposite sign round about a state of equilibrium which is never re-established after it has once been disturbed. It may be that the material inequalities, whilst retaining a constant sum, are continually undergoing modifications.

By means of empirical relations, the author has calculated the atomic weights of the first elements in the vertical columns from the atomic weight of hydrogen, with a view to obtain their absolute values. One of these relations leads to the following values.

	H = 1.	O = 16.		H = 1.	O = 16.
Beryllium.	9.0156250	9.05098	Oxygen.	15.9375000	16.00000
Lithium ..	6.9921875	7.01961	Nitrogen	13.9843750	14.03922
( $\beta$ ) .....	3.8906250	3.90588	Carbon.	11.9453125	11.99216
( $\alpha$ ) .....	2.9375000	2.94902	Boron ..	10.9218750	10.96471

Friedel states that, several days before April 22, Boisbaudran spoke of 20 and 3.9 as the probable atomic weights of argon and helium respectively.

C. H. B.

**The Colour of Atoms, Ions, and Molecules.** By M. CAREY LEA (*Zeit. anorg. Chem.*, 1895, 9, 312—328; also *Amer. J. Sci.*, 49, 357—374).—When the elements are divided into two series, one containing those elements whose atoms show colour in combination, the other containing those elements whose atoms in certain cases, or

in all cases, show no colour, it is seen that this classification corresponds in a remarkable degree with the chemical properties of the elements.

It has been shown by Ewan that a solution of copper sulphate containing 2.38 gram-equivalents per litre, in which the dissociation amounts to 15.3 per cent., has almost the same absorption for light as a solution containing 0.2856 gram-equivalent per litre, in which the dissociation amounts to 31.7 per cent. Therefore, the colour is not due to the free ions or to the molecules, and must be due to the atoms, whether they be present as ions or combined with another ion to form an electrolyte. Thus, in dilute solutions of cobalt salts, the ions show the characteristic colour of cobalt, and cobalt cyanide which contains no water also shows the same colour. The same is true of nickel cyanide.

In an electrolyte which gives a colourless solution in water, both the cation and anion are colourless. Thus, lithium bromide, which gives a colourless solution, contains the colourless ions of lithium and bromine. There is no connection between the colour of an atom and the colour of the element formed by a combination of atoms; thus the colourless bromine atom forms the intensely coloured element bromine. The colourless nature of the bromine atom may be inferred from the fact that all its compounds with the alkalis and alkaline earths are colourless. In an electrolyte which gives a coloured solution in water, when the anion is a single atom, the colour is due to the cation, for all elementary anions are colourless. Even if the anion is a complex one, such as  $\text{SO}_4$ , and is colourless, the colour of a solution of an electrolyte containing this anion is to be referred to the cation.

The colour, or want of colour, of the atom of an element is a function of its atomic weight. Elements with atomic weights up to 47 have only colourless ions; then follow eight elements, Ti, V, Cr, Mn, Fe, Co, Ni, Cu with coloured ions; nine elements, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Yt with colourless ions; six metals, Nb, Mo, Ru, Rh, Pd, Ag with coloured ions; nine metals, Cd, In, Sn, Sb, Te, I, Cs, Ba, La with colourless ions; ten metals, Ce, Di, Sm, Er, Ta, W, Os, Ir, Pt, Au with coloured ions; and finally the six metals, Hg colourless, Tl coloured, Pb colourless, Bi coloured, Th colourless, and U coloured.

The author has arranged the elements in a periodic system, on the basis that no element which in all its combinations shows coloured ions can be combined in the same natural group with elements which have colourless ions.

The elements which have colourless ions can be arranged in nine horizontal groups, in which each element falls naturally into its proper place. This division of the elements contains all those whose ions can act as anions. Elements which have only coloured ions can be arranged similarly in five vertical series, the last series containing only the element uranium. This division contains elements whose ions can act only as cations. There remain eleven elements, Ti, V, Cu, Nb, Mo, Ag, Ce, Ta, W, Tl, Bi, whose ions are in some cases coloured, in others colourless. In the whole series of all the elements, these elements come between a group of elements which have colour-



less ions and one of elements which have coloured ions. There is no case in which an element with only colourless atoms falls in the periodic series between one of these eleven elements and an element with only coloured atoms. And also an element with only coloured atoms never comes between one of these eleven elements and one with only colourless atoms.

The conclusion is that the colour of the elementary atoms is a function of the atomic weight. Atoms with the atomic weight 1—47 are colourless, 52—59 coloured, 65—90 colourless, 103—106 coloured, 112—139 colourless, 145—169 coloured, 192—196 colourless. Elements which have atomic weights which lie between these groups have both colourless and coloured atoms.

E. C. R.

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## Inorganic Chemistry.

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**Composition of Atmospheres which Extinguish Flame.** By FRANK CLOWES (*Proc. Roy. Soc.*, 1894, **56**, 2—6).—The experimental flame burning at a platinum jet 1 mm. in diameter, was 0.75 in. in height; it was gradually lowered into a cylinder containing the atmosphere of mixed gases, and these were considered to be in extinctive proportions if the flame was extinguished during its downward passage, or immediately on attaining its lowest position in the cylinder. The gaseous mixture was regarded as containing the minimum quantity of extinctive gas, when the flame on being lowered into another mixture containing 1 per cent. less of such gas continued to burn in it for a few seconds before being extinguished. Experiments made with flames of hydrogen and alcohol, varying from 0.4 in. to 1.5 in. in height, show that the varying dimensions of the flame are without influence on the proportion of carbonic anhydride in the air necessary to produce extinction. Characteristic differences were observed between the behaviour of wick-fed flames and that of gas-fed flames when they were introduced into an atmosphere which extinguished them, the wick-fed flames gradually diminishing in size until they vanished, whilst the gas-fed flames gradually increased in size, becoming paler and apparently lower in temperature until they suddenly expired.

The results of the experiments, of which a table is given in the original paper, show (1) that the extinction of a flame is not determined simply by the proportion which the inert gas bears to the oxygen of the atmosphere into which it is introduced, but that the nature of the inert gas present also influences the result. (2) Carbonic anhydride exerts a more powerful extinctive effect on flame than nitrogen does. (3) There is a remarkable uniformity in the proportions of inert gas, which must be mixed with air in order to just extinguish wick-fed flames; but this uniformity does not apply to the flames of combustible gases burnt from a jet. (4) The flames of gases burnt from a jet show no simple relation, as regards the proportion of oxygen present

in the extinctive atmosphere, to the relative proportions of oxygen required for their complete combustion. In the presence of the hydrogen flame carbonic anhydride does not suffer partial deoxidation.

The introduction of a minimum of 15 per cent. of carbonic anhydride into air is necessary to cause it to extinguish ordinary wick-fed flames. For the extinction of coal-gas flames, however, the addition of 33 per cent. of carbonic anhydride is necessary, and for the hydrogen flame 58 per cent.

E. C. R.

**Preparation of Perchloric acid and its Use in the Estimation of Potassium.** By D. ALBERT KREIDER (*Zeit. anorg. Chem.*, 1895, 9, 342—348).—Sodium chlorate is converted into perchlorate by cautiously heating during  $1\frac{1}{2}$ —2 hours, the residue being dissolved in water, and hydrochloric acid added in quantity sufficient to decompose any unaltered chlorate; the solution is then evaporated to dryness, stirring vigorously towards the end of the operation, as otherwise the perchlorate retains some water and solidifies so that it cannot be removed from the dish. The finely pulverised residue is treated with concentrated hydrochloric acid, filtered from the sodium chloride, and well washed with hydrochloric acid, which is then removed from the solution by evaporation. The perchloric acid is sufficiently pure for the determination of potassium, for the slight residue obtained when it is evaporated is completely soluble in alcohol (97 per cent.), and consists of sodium perchlorate. If the sodium chlorate contained potassium chlorate the pulverised crystals of chloride and perchlorate are treated with alcohol (97 per cent.), which dissolves the latter more readily than the former, the alcohol is removed, and the residue treated with hydrochloric acid as above. The solubility of sodium perchlorate in alcohol (97 per cent.) is 0.2 gram per c.c. The preparation of perchloric acid, including the separation of the potassium salts, occupies about two days; 100—300 grams of sodium chlorate may be conveniently employed. For the estimation of potassium, the substance, which must be free from sulphuric acid, is dissolved in hot water (20 c.c.), perchloric acid (1.5 times the theoretical quantity) added, and the solution evaporated to a syrup, stirring constantly. It is then again dissolved in water and evaporated, the residue being washed twice with about 20 c.c. of 97 per cent. alcohol containing 0.2 per cent. of perchloric acid, the alcohol is decanted through an asbestos filter, the crystals dissolved in hot water (10 c.c.) containing a little perchloric acid, and the solution again evaporated to dryness; the residue is finally washed on to the filter with the smallest possible quantity of the alcoholic perchloric acid, treated once with pure alcohol, dried at  $130^{\circ}$ , and weighed. The alcoholic washings should not exceed 50—70 c.c. The removal of phosphoric acid is unnecessary, but if it is present the potassium perchlorate should remain in contact with perchloric acid, in excess, before treating with alcohol. The analytical results are satisfactory.

J. B. T.

**Density of Nitrogen.** By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1894, 55, 340—344).—In a previous paper (*Proc. Roy. Soc.*, 53, 146), the

author has shown that nitrogen prepared by Lupton's method is lighter, by about 1/1000 part, than that derived from air in the usual way. It is now shown that nitrogen derived entirely from chemical compounds is materially lighter than atmospheric nitrogen. This difference amounts to about 1/200 part of the whole.

	Mean density.
Nitrogen from nitric oxide by hot iron.....	2.30008
Nitrogen from nitrous oxide by hot iron .....	2.29904
Nitrogen from ammonium nitrite by hot iron ....	2.29869
Atmospheric nitrogen by hot copper (1892).....	2.31026
Atmospheric nitrogen by hot iron (1893).....	2.31003
Atmospheric nitrogen by ferrous hydrate (1894)..	2.31020

Experiments have proved that the densities do not alter when the gas is exposed to the silent electric discharge. The author demonstrates that the lightness of the nitrogen from chemical compounds cannot be due to the presence of impurities such as hydrogen, ammonia, water vapour, &c.

J. J. S.

**Reduction of Nitric Oxide by Moist Iron or Zinc.** By PAUL SABATIER and J. B. SENDERENS (*Compt. rend.*, 1895, 120, 1158—1161).—Nitric oxide in contact with moist zinc turnings over water is at first reduced to a mixture of nitrous oxide and nitrogen with a small quantity of hydrogen. If the action is allowed to continue, the proportion of nitrous oxide diminishes, whilst that of nitrogen and hydrogen increases, the gas finally being a mixture of nitrogen and hydrogen only. The hydrogen is doubtless a result of the action of the ammonia on the zinc.

In contact with moist iron, standing over mercury, the nitric oxide is reduced to a mixture of nitrous oxide and nitrogen, in the proportion of 2 vols. of the former and 1 vol. of the latter, with a small quantity of hydrogen, which results most probably from the action of the iron on the water in presence of mercury.

The reduction of the nitric oxide takes place slowly, probably because of its slight solubility in water. A solution of the gas in ferrous sulphate solution is much more rapidly reduced, and the gas produced consists at first of 2 vols. of nitrous oxide with 1 vol. of nitrogen, but after a time the proportion of nitrous oxide diminishes and that of nitrogen increases, whilst hydrogen is also given off in gradually increasing proportion, until at the end of the action the gas is a mixture of nitrogen and hydrogen only in practically equal volumes. The iron becomes covered with hydrated ferrous-ferrie oxide. Similar results are obtained with zinc.

C. H. B.

**New Polyphosphoric Acid,  $H_5P_3O_{10}$ , and its Salts.** By FRITZ SCHWARZ (*Zeit. anorg. Chem.*, 1895, 9, 249—266).—Salts of tetraphosphoric acid have been described by Fleitmann and Henneberg (*Annalen*, 65, 322), the sodium salt being obtained by melting the anhydrous pyrophosphate with hexametaphosphate. It crystallises with  $36H_2O$ . Fleitmann and Henneberg's acid tetraphosphate,  $Na_4H_2P_4O_{13}$ , is formed from the salt  $Na_2H_2P_2O_7$  by the removal of the water of crystallisation.

*Sodium triphosphate* is best obtained by melting 100 grams of the pyrophosphate with 50—55 grams of metaphosphate; after keeping it in a fused state for about 15 minutes, it is allowed to cool slowly, and the product is broken into small pieces and cautiously dissolved in cold water. The solution, allowed to remain all night, is filtered, and the filtrate evaporated spontaneously; the crystals which are deposited can be recrystallised from cold water, but great care is necessary, as the heat developed on treating them with water is sufficient to partially convert the salt into metaphosphate. It crystallises from water with  $16\text{H}_2\text{O}$  in transparent crusts, loses water on exposure to air, and is very soluble. The solution has a faintly alkaline reaction; when boiled, it is quickly converted into pyrophosphate, whilst with mineral acids and some organic acids it yields pyrophosphate in the cold, and also orthophosphate when heated with them. The solution gives no precipitate with magnesia mixture until strong ammonia is added, which converts the salt into orthophosphate. Triphosphoric acid gives precipitates with salts of the heavy metals only in very concentrated solutions, and is then only partially precipitated, whereas pyrophosphoric acid is completely precipitated by salts of the heavy metals even in dilute solutions. The reason of this characteristic behaviour of triphosphoric acid lies in the formation of double salts; these separate in well-formed crystals from concentrated solution of the sodium salt and the salt of the heavy metal. The free acid obtained from the copper salt by means of hydrogen sulphide is quickly converted, in aqueous solution, into pyrophosphoric acid, and consequently albumin is not coagulated by the solution. If however, a few drops of acetic acid are added to a solution of the sodium salt, the triphosphoric acid in the nascent state will coagulate albumin.

*Cobalt sodium triphosphate*,  $\text{CoNa}_3\text{P}_3\text{O}_{10} + 12\text{H}_2\text{O}$ , is obtained by adding a solution of a cobalt salt to one of sodium triphosphate of such a strength that no precipitate is formed, and then evaporating the mixed solution in a vacuum; it crystallises in beautiful, lustrous, rose-red crystals, which when dehydrated turn blue, and melt at a red heat to a clear blue glass. It is insoluble in water, but easily soluble in acids, by which, however, it is not decomposed. A salt of the composition  $4\text{CoO}, \text{Na}_2\text{O}, 3\text{P}_2\text{O}_5$ , is obtained as a rose-red precipitate on adding cobalt sulphate (1.5—1.75 grams) to sodium triphosphate (1 gram) dissolved in the smallest possible quantity of water; it contains 29—33 per cent. of water.

*Nickel sodium triphosphate*,  $\text{NiNa}_3\text{P}_3\text{O}_{10} + 12\text{H}_2\text{O}$ , obtained in a similar way to the cobalt salt, forms green crystals which turn yellow when heated, and melts at a red heat to a brown glass. These nickel and cobalt salts crystallise in rhombic prisms and are isomorphous.

*Copper triphosphate*,  $5\text{CuO}, 3\text{P}_2\text{O}_5 + 13\text{H}_2\text{O}$ , is obtained by precipitating the sodium salt with copper sulphate in concentrated solution.

*Lead triphosphate*,  $6\text{PbO}, 4\text{P}_2\text{O}_5$ , is obtained as a white precipitate which dissolves in an excess of the sodium salt; at a high temperature it melts to a white glass. The precipitate of this salt is always mixed with lead tetraphosphate.

*Barium triphosphate and calcium triphosphate*, obtained by adding

barium chloride and calcium chloride respectively to the solution of the sodium salt, form thick, flocculent, white precipitates.

*Zinc sodium triphosphate*,  $4\text{ZnO}, \text{Na}_2\text{O}, 3\text{P}_2\text{O}_5 + 19\text{H}_2\text{O}$ , is very similar to the cobalt and nickel salts; it is obtained from concentrated solutions as a white, crystalline powder, and from dilute solutions in beautiful, prismatic, colourless crystals. At a high temperature, it melts to a colourless glass. E. C. R.

**Reduction of Silica by Aluminium.** By VIGOUROUX (*Compt. rend.*, 1895, **120**, 1161—1164).—When finely powdered silica (3 mols.) and finely powdered aluminium (4 atoms), previously freed from grease, are heated together, there is brilliant incandescence, the silica is reduced, and, after successive treatments with hydrochloric, sulphuric, and hydrofluoric acids, amorphous silicon is obtained.

Crystallised silicon is obtained on heating silica and aluminium in an electric furnace. If the aluminium is in excess, the silicon dissolves in it; if the silica is in excess, the silicon forms the lower layer in the carbon crucible, or partly fuses and partly distils if the tube furnace is used. It can also be obtained in large quantity by heating a mixture of silica and aluminium with potassium silicofluoride in a carbon crucible in a Perrot furnace. By whichever method it is obtained, crystallised silicon forms thin, hexagonal lamellæ, which are sometimes very thin, and then are transparent, and have a yellow colour, but do not act on polarised light. The chemical properties of the crystallised silicon are identical with those of the amorphous variety (this vol., ii, 263). C. H. B.

**A Remarkable Change of Structure in Glass when Heated.** By ED. PŘIWOZNÍK (*Zeit. anorg. Chem.*, 1895, **9**, 289—290).—The author describes the exfoliation which some specimens of soda glass undergo when heated.

**Molecular Weight of Mercurous Chloride.** By MICHELE FILETTI (*Gazzetta*, 1895, **25**, i, 88—94).—A polemical paper replying to V. Meyer (this vol., ii, 46), who has already published his answer (this vol., ii, 166). W. J. P.

**Crystalline Aluminium Chloride.** By L. M. DENNIS (*Zeit. anorg. Chem.*, 1895, **9**, 339—341).—In order to obtain crystalline aluminium chloride, commercial anhydrous aluminium chloride is dissolved in water, and, after being filtered through glass wool, is mixed with concentrated hydrochloric acid, and the solution, cooled with a freezing mixture, is saturated with dry hydrogen chloride. The crystals which rapidly form are washed by decantation with concentrated hydrochloric acid until free from iron, and the excess of acid is removed as far as possible by the aid of the pump. The crystals are then placed on porous tiles and exposed to the air until free from hydrogen chloride; in moist air, water is absorbed, but if kept at 20° their weight becomes constant after about 48 hours. The crystals,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , do not change when kept over sulphuric acid, but if heated in a stream of dry hydrogen chloride, a basic salt

is formed. Crystals may be obtained by adding concentrated hydrochloric acid to cold, concentrated, aluminium chloride solution, but they are very small. The larger crystals, which are fully described, consist of hexagonal prisms of the second order, bounded by rhombohedral faces,  $a:c = 1:0.5356$ ;  $p:r = 62^\circ 54'$ ;  $r:r = 54^\circ 12'$ . The refractive index = about 1.6; the double refraction is strong  $\omega - \epsilon = 0.053$ .  
J. B. T.

**Preparation of Stannic Bromide.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1895, 9, 365—368).—Tin, in pieces 2—3 cm. long, is placed in a distillation flask, closed at the top with a cork fitted with a separating funnel drawn out to a capillary point; the funnel is filled with bromine, which is added to the tin so slowly that the temperature remains at  $35$ — $59^\circ$ , and the side tube does not become filled with bromine vapour; the action proceeds quietly. When the greater portion of the tin has disappeared, the contents of the flask are distilled; the first few drops contain a little bromine, but that which subsequently passes over is pure stannic bromide. It boils at  $201^\circ$ , is colourless, readily forms crystals, and fumes slightly on exposure to moist air. The bromide may be stored in a corked flask; if this is heated to about  $40^\circ$ , the bromide readily melts, and can be withdrawn in any desired quantity.  
J. B. T.

**The two Modifications of Stannic acid.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1895, 9, 369—381).—A historical account of the investigation of stannic acid and metastannic acid is given; the gradual and almost equal loss of water by both compounds under similar conditions is confirmed, proving that their composition is identical, and that both exist in all degrees of hydration, from  $H_4SnO_4$  to  $H_2SnO_3$ . The compounds retain their characteristic properties after repeated precipitation from salts or solutions, and their salts differ. Recently prepared aqueous solution of stannic chloride or bromide is identical with that formed by dissolving stannic acid in hydrochloric acid or hydrobromic acid respectively. Aqueous stannic chloride solution gradually changes when kept, and the course of this change may be followed by means of potassium ferrocyanide; it consists in a progressive decrease of the tin ions. Aqueous stannic bromide solutions gradually deposit a white gelatinous precipitate, and the change which takes place in the solution appears to proceed regularly, as represented by the expression,  $\frac{1}{t} \log \frac{a}{a-x} = K$  constant, where  $a$  = the tin in the stannic bromide,  $x$  = the tin in the precipitated metastannic acid,  $H_4SnO_4$ , and  $t$  = the time in minutes. The value of  $K$  found =  $0.000726$ — $0.000906$ ,  $t = 1430$ — $3890$ . In one case  $K = 0.001071$ ,  $t = 1010$ , the difference between this value and those given above is probably due to incomplete precipitation of the metastannic acid.  
J. B. T.

**Cerite Earths.** By PAUL SCHUTZENBERGER (*Compt. rend.*, 1895, 120, 1143—1147).—The methods previously employed (this vol., ii, 352) have been extended to the nitrates remaining undecomposed in

presence of excess of potassium nitrate after complete elimination of the cerium. These nitrates were fractionated by heating them at gradually increasing temperatures, and the treatment was repeated on some of the first products of the fractionation. The general result is that the curve of the atomic weights of the metals contained in the successive fractions rises from a minimum of about 135 to a maximum of 143 to 143·5, and then descends to a second minimum of about 138. The maximum atomic weight of didymium lies between 143 and 143·5. When monazite is subjected to the same treatment as cerite, the oxides which separate from the fused nitrates between  $410^{\circ}$  and  $460^{\circ}$ , after careful elimination of the cerium, form decidedly rose-coloured salts, which show the absorption bands of neodymium, and contain a metal with an atomic weight very near 137·5. There are reasons for believing that between the two limits of 143·5 and 137·5 there are other metals which have all the general properties of didymium, and in particular an element with an atomic weight of about 140.

Lanthanum oxide (as defined subsequently) can be split up into at least two oxides, the one containing a metal with an atomic weight of about 138, and the other a metal of atomic weight of about 135. As in the case of didymium, the stability of the nitrates when heated is higher the lower the atomic weight of the metal.

The author defines as *cerite earths* all the oxides which give a double potassium sulphate insoluble in a saturated solution of potassium sulphate; as *cerite oxides* all the oxides capable of conversion into a dioxide, and forming colourless salts, the solutions of which show no absorption bands; as *didymium oxides* all those which form more or less rose-coloured salts, the solutions of which show the absorption bands of didymium salts, the oxide formed at high temperatures being  $M_2O_3$ ; and as *lanthanum oxides* those which form colourless deliquescent salts, with no absorption bands, and yield an oxide,  $M_2O_3$ , when strongly heated. (Compare Schutzenberger, *loc. cit.*, and Brauner, *ibid.*) C. H. B.

**Iodine Compounds of Lead with Excess of Iodine.** By HORACE L. WELLS (*Zeit. anorg. Chem.*, 1895, **9**, 304—311, and *Amer. J. Sci.*, **50**, 21—26).—The salt,  $5Pb(OAc)_2 \cdot 3KI \cdot 6I$ , which has been prepared by Johnson (*Trans.*, 1878, 189) by mixing a hot, concentrated, alcoholic solution of potassium triiodide with a hot, saturated solution of lead acetate, has been examined by the author. It is formed when 30 grams of potassium iodide and 50 grams of iodine dissolved in absolute alcohol are mixed with 40—100 grams of crystallised lead acetate also dissolved in alcohol, separating in crusts or groups of larger crystals, which are fairly stable when exposed to the air. The lead and potassium are determined in the salt by dissolving it in dilute nitric acid, precipitating the lead as sulphate, and estimating the potassium in the filtrate also as sulphate; the iodine is determined by treating the salt with a solution of sodium arsenite, acidifying with nitric acid, and then adding excess of silver nitrate.

The salt,  $Pb_2I_5(OH)_2$ , previously described by Gröger, but to which he assigned the formula  $Pb_2I_5O$ , has also been examined. It is



most easily obtained by mixing a solution of 10 grams of iodine in 100 c.c. of absolute alcohol, with a solution of 50 grams of crystallised lead acetate in 150 c.c. of water, 3 c.c. of acetic acid, and 300 c.c. of absolute alcohol; after 14—16 hours, it is filtered from a slight precipitate and diluted with 1.5 litres of boiling water. On cooling, the salt crystallises out in lustrous, black octahedra, which are fairly stable when exposed to the air; it is not decomposed by cold water, or by alcohol. Using Gröger's method, the salt is obtained as a reddish-brown powder, but it has the same composition as the crystalline salt.

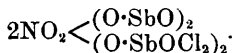
E. C. R.

**Reactions of Lead Sulphide.** By ARTHUR LODIN (*Compt. rend.*, 1895, **120**, 1164—1167).—Lead sulphate, alone, or mixed with other substances, was heated in a glass or porcelain tube, the temperatures being measured by means of a Le Chatelier thermoelectric couple. When heated at 860° in a current of carbonic anhydride, lead sulphide volatilises to a considerable extent, and at the same time is partially oxidised; in a current of nitrogen, it volatilises completely at 860°, without previously melting. The melting point of the sulphide when rapidly heated is between 930° and 940°. Mixtures of the sulphide with the monoxide, or the sulphate, when heated in porcelain tubes in an atmosphere of nitrogen, gave results which confirm the accuracy of the ordinary equations,  $\text{PbS} + 2\text{PbO} = 3\text{Pb} + \text{SO}_2$ ;  $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ ; and  $\text{PbS} + 3\text{PbSO}_4 = 4\text{PbO} + 4\text{SO}_2$ .

Although lead sulphide only melts at 935°, it has a very considerable vapour tension even at much lower temperatures, and this fact explains not only the phenomena of volatilisation, which Hannay attributed to the formation of a hypothetical compound,  $\text{PbS}_2\text{O}_2$  (*Proc.*, 1894, 113 and 151), but also the interactions between the sulphide on the one hand, and the oxide or sulphate on the other, at temperatures below 935°.

C. H. B.

**Action of Nitric Peroxide on Antimony Salts.** By VINCENT THOMAS (*Compt. rend.*, 1895, **120**, 1115—1117).—The action of nitric peroxide on a solution of antimony trichloride in chloroform yields a white, somewhat stable, compound of the composition  $\text{Sb}_4\text{O}_{11}\text{N}_2\text{Cl}_4$ , probably  $2\text{SbO}_2$ ,  $2\text{SbOCl}_2$ ,  $\text{N}_2\text{O}_5$ , or



Antimony tribromide, under the same conditions, yields the white compound,  $\text{Sb}_4\text{O}_{13}\text{N}_4$  or  $\text{N}_2\text{O}_5 \cdot 2\text{Sb}_2\text{O}_3$ , analogous to the compound  $2\text{Sb}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$ , obtained by Peligot by the combination of nitric and antimonious anhydrides.

C. H. B.

**Salts of Amidochromic acid.** By ALFRED WERNER and A. KLEIN (*Zeit. anorg. Chem.*, 1895, **9**, 291—294).—The authors have endeavoured to prepare potassium amidochromate,  $\text{KCrO}_3\text{NH}_2$ , and the compound,  $\text{Cr}_2\text{O}_3\text{H}_2\text{N}$ , described by Heintze (*J. pr. Chem.*, **4**, 216), as obtained by the action of dry ammonia on potassium chlorochromate. The authors, however, following strictly the conditions laid down by

Heintze, obtained nothing but potassium dichromate, and they were not more successful when they modified his method. E. C. R.

**Conductivity of Permanganic acid.** By JOH. M. LOVÉN (*Zeit. physikal. Chem.*, 1895, **17**, 374—376).—Owing to the publication of work by Franke on the conductivity of permanganic acid, the author claims priority of determination and publication. The values for the conductivity given increase from 315 at  $V = 2$  to 378 at  $V = 256$ , after which it remains constant; the value at infinite dilution given by Franke was 383·8. The numbers are in general higher than those of Franke, this being attributed to the precautions taken by the author to prevent the decomposition of the acid by the platinum black. L. M. J.

**Nitroso-compounds of Iron.** By KARL A. HOFMANN and O. F. WIEDE (*Zeit. anorg. Chem.*, 1895, **9**, 295—303).—The authors have already described salts of dinitrosoferrothiosulphonic acid (this vol., ii, 317), and the method by which they can be prepared; other salts have now been obtained. The *rubidium salt*,  $\text{Fe}(\text{NO})_2\text{S}_2\text{O}_3\text{Rb} + \text{H}_2\text{O}$ , obtained by adding rubidium chloride to a solution of the sodium salt, crystallises in lustrous, black needles, and is less soluble than the sodium salt. The *cæsium salt* crystallises without water in lustrous, black crystals, and is sparingly soluble. The authors were unable to obtain a thallium salt corresponding with the preceding; this non-formation of a thallium salt affords a characteristic distinction between dinitrosoferrothiosulphonic acid and heptanitrosoferrothiosulphonic acid, the latter yielding a very characteristic thallium salt of the composition  $\text{Fe}_4(\text{NO})_7\text{S}_3\text{Tl}$ .

The thio-group in dinitrosoferrothiosulphonic acid is very easily eliminated, and, when a solution of the sodium salt is boiled as long as gas is evolved, the sodium salt of the hepta-acid is formed; this crystallises in needles, and may be characterised by converting it into the thallium salt. *Cæsium heptanitrosoferrothiosulphonic acid*,  $\text{Fe}_4(\text{NO})_7\text{S}_3\text{Cs}\cdot\text{H}_2\text{O}$ , obtained by adding cæsium chloride to a solution of the sodium salt, separates as a black, crystalline powder, and is very sparingly soluble. The *rubidium salt* with  $1\text{H}_2\text{O}$  is obtained as a black, crystalline powder.

The *ammonium salt*,  $\text{Fe}_4(\text{NO})_7\text{S}_3(\text{NH}_4)\cdot\text{H}_2\text{O}$ , is obtained by passing nitrous oxide into freshly precipitated ferrous sulphide suspended in water, or into a mixture of ferrous hydroxide, ferrous sulphate, and carbon bisulphide saturated with ammonia, and also by passing the gas into a mixture of ferrous hydroxide and carbon bisulphide. The salt, extracted from the product of the action by hot alcohol, crystallises in lustrous, black needles; when distilled with soda, it yields more than the theoretical quantity of ammonia, because some of the nitrous oxide is also converted into ammonia. Heptanitrosoferrothiosulphonic acid is easily detected by converting it into the characteristic cæsium salt.

The *compound*,  $\text{Fe}(\text{NO})_2\text{SEt}$ , is obtained by treating a mixture of ferrous sulphate, potassium hydroxide, water, and ethylic mercaptan with nitrous oxide; it crystallises from absolute alcohol in large,

lustrous, black, six-sided plates, has no odour, melts at  $78^{\circ}$  to a brownish-black liquid, is volatile at higher temperatures, and is insoluble in water. Determinations of the molecular weight gave numbers varying from 341 to 356, whilst the formula,  $[\text{Fe}(\text{NO})_2\text{SEt}]_2$ , = 354.

*Dinitrosoferrophenyl mercaptide*,  $\text{Fe}(\text{NO})_2\text{SPh}$ , is obtained, together with a large quantity of phenylic bisulphide, when a mixture of ferrous sulphate, potassium hydroxide, water, and thiophenol is treated with nitrous oxide. It crystallises from benzene in lustrous, black leaflets, and melts at  $179^{\circ}$ . The two preceding compounds are very stable.

E. C. R.

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## Physiological Chemistry.

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**The Output of Carbonic acid and Temperature.** By MARCUS S. PEMBREY (*J. Physiol.*, 1895, 363—379). **Heat Regulation in Hybernating Animals.** By MARCUS S. PEMBREY and W. HALE WHITE (*Proc. Physiol. Soc.*, 1895, 35—37).—Further details and full account of experiments similar to those already published in preliminary communications (compare this vol., ii, 51). W. D. H.

**An Ideal Circulating Fluid for the Isolated Frog's Heart.** By F. S. LOCKE (*J. Physiol.*, 1895, 18, 332—333).—An ideal fluid for this purpose must, according to Albanese (*Arch. exp. Path. Pharm.*, 32, 297), possess (1) isotony with frog's blood; (2) a certain amount of viscosity; (3) a degree of alkalinity sufficient to remove the acid products of metabolism; and (4) a supply of free oxygen. These conditions are all fulfilled by a solution containing 0.6 per cent. of sodium chloride, 2 per cent. of ordinary gum arabic, and a trace of sodium carbonate and kept saturated with oxygen by passing a stream of the gas through it. Gum arabic contains the potassium, magnesium, and calcium salts of arabic and similar acids; the potassium and calcium present appear to be necessary, as Ringer has stated, although denied by the Strassburg school. W. D. H.

**Comparative Digestibility of Sugar Beet, Mangel Wurzel, and Distillery Roots.** By PAUL GAY (*Ann. Agron.*, 1895, 21, 145—171).—Experiments were made in which a sheep was fed for three successive periods of two weeks each with lucerne (0.5 kilo.), oats (0.25 kilo.), together with mangel wurzel (3 kilos.), distillery roots (1.953 kilos.), and sugar beet (1.648 kilos.) respectively. The different amounts of the three roots represent the same amounts of dry matter. The actual amounts of food constituents consumed and the composition and amounts of excrement were determined, and from the results the amounts digested were calculated. The following table gives the coefficients of digestibility of the three roots, (1) mangel wurzel, (2) distillery roots, (3) sugar beets, and their nutritive relation.

	Total.	Coefficients of digestibility.					Nutritive relation.
		Protein.	Ether extract.	Nitrogen free extract.	Cellulose.	Ash.	
1	72·94	77·03	55·64	82·81	56·55	35·14	1/4·4
2	76·68	77·14	71·49	86·07	52·53	38·19	1/11·3
3	73·56	74·27	67·95	82·41	52·45	40·04	1/11·9

The results show clearly the superiority of distillery roots over both sugar beet and mangel wurzel. This rather unexpected result is explained by a consideration of the absolute and relative digestibilities, which depend respectively on the natural diffusibility of the food constituents, and on the relation between the proteids on the one hand and the ethereal extract and nitrogen free extract on the other. The mean digestibility, a judicious combination of absolute and relative digestibility, gives the probable nutritive value of a food (compare Dehérain, *Abstr.*, 1891, 493, and *Ann. Agron.*, 1892, 18, 380).  
N. H. J. M.

**Mycological Processes in the Intestines.** By VINCENT D. HARRIS (*J. Pathol. and Bacteriol.*, 1895, 3, 310—321).—The numerous species of bacteria met with in the intestines fall into two main groups: (a) those of the intestine, and (b) those in the intestine, whose presence is more or less accidental. Those in the first class are comparatively few in number. The chief of these which were isolated are described, and their chemical action investigated. Of the 20 species examined, only six produced indole in the test time of 24 hours; of these, four belong to the *B. coli communis* class. In no case was leucine or tyrosine obtainable from the nutrient material. The precipitation of the caseinogen of milk is a fairly common action; much commoner than a conversion of caseinogen into casein. In one case, the caseinogen was converted into a soluble proteid (proteose or peptone) without any preliminary curdling or precipitation. Although so many of the bacteria isolated grow readily on potato, very few of the intestinal bacteria can convert starch into sugar; the process on the potato probably stops at the dextrin stage. The inversion of cane sugar was only found to occur with one variety; a more frequent action on cane sugar appears to be the formation of lactic acid, and probably of butyric acid too. The formation of peptone and the hydrolysis of fats are extremely rare mycological actions in the intestines.  
W. D. H.

**Feeding with Grain.** By O. BÖTTCHER (*Bied. Centr.*, 1895, 24, 377—382).—The money-values of the digestible food units of a number of grains and cattle foods are calculated from their percentage composition, and the relative money-values of protein, fat, and carbohydrates, which are at present (Emmerling) as 3 : 3 : 1. The results show that even with the present low prices of grain, a food

unit is considerably dearer in the form of grain than in the ordinary commercial foods. Moreover, owing to the comparatively low percentage of protein and fat in grains, they could not be employed as substitutes for the commercial foods without waste of carbohydrates.

In a wet season, when much grain is spoilt, the good should be carefully separated, and the damaged grain given to cattle after being steamed, or else treated with 2 per cent. sulphuric acid (Maercker) to destroy injurious fungi. In feeding such grain, only small amounts should be given in conjunction with hay, roots, &c.; proteids may advantageously be added in the form of earth nut or cotton meal, or, still better, meat meal. Meat meal is not, as sometimes supposed, injurious to the health of cattle or to the quality of the meat, or even to that of the milk and butter, if given in small quantities (0.75 kilo.).

N. H. J. M.

**Absorption and Metabolism in Obstruction of the Pancreatic Duct.** By VAUGHAN HARLEY (*J. Pathol. and Bacteriol.*, 1895, 3, 245—258).—Obstruction of the pancreatic duct in man, like the partial extirpation of the gland in animals, gives rise to no glycosuria, and in the present paper a comparison of a case of this condition in man, with that produced in dogs in which the organ has been wholly or partly extirpated, shows that the alterations in metabolism correspond. There is a greatly diminished absorption of the fat given in the food, and at the same time proteid absorption is also greatly lessened. Excess of food must be therefore given, otherwise emaciation occurs. Tables of analyses accompany the paper.

W. D. H.

**Synthesised Colloids and Coagulation.** By JOHN W. PICKERING and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1895, 18, 285—305; compare Abstr., this vol., i, 484).—This paper deals especially with the physiological effect of these substances when injected intravenously. The main effect in rabbits, dogs, cats, guinea pigs, and rats resembles that of nucleo-proteids producing extensive intravascular coagulation. They do not apparently (like snake poison) cause destruction to the endothelial lining of the vascular wall, neither are they destructive to blood corpuscles. The resemblance of their action to that of nucleo-proteids is borne out even in minor points, such as that they do not cause clotting in the intravascular blood of albino rabbits; in dogs small doses induce a "negative phase." They kill apparently by their action on the respiratory centre. It is suggested that the action of these materials is to be explained partly by their colloid nature, but more particularly by their containing an intramolecular group of the amido-fatty series in a high state of condensation. The similar action of nucleo-proteids is probably to be explained in the same way.

W. D. H.

**Neurine in Blood.** By FRANCESCO MARINO-ZUCCO and C. MARTINI (*Gazzetta*, 1895, 25, i, 101—104).—Owing to the ease with which lecithin decomposes, no positive proof has yet been given of the existence of neurine as such in arterial blood; the authors have, however, devised a method by which the neurine and lecithin may be separated from

blood under conditions which render it impossible that the neurine could result from the decomposition of the lecithin during the process employed.

About 3 litres of ox blood, freshly drawn from the jugular, are well agitated with a mixture (6 litres) of alcohol and ether (1 : 2); the alcoholic liquid is then treated with excess of an ethereal acid solution of platinic chloride, and water added until the ether separates. The latter is then drawn off, and the aqueous liquid repeatedly extracted with ether; the united ethereal solutions contain the lecithin whilst the aqueous liquor contains the neurine platinochloride; since no phosphoric acid can be detected in the aqueous solution, it follows that the neurine does not occur as a decomposition product of the lecithin. After precipitating the platinum as sulphide, heating the filtered liquor with precipitated lead oxide, and separating the lead as sulphide, a syrup is obtained from which neurine may be isolated as the aurochloride.

W. J. P.

**Proteoses in Serous Effusions.** By WILLIAM D. HALLIBURTON and P. C. COLLS (*J. Pathol. and Bacteriol.*, 1895, 3, 295—299).—In searching for proteose or peptone in such fluids as blood, milk, and serous effusions, it is important to use such methods as will not in themselves lead to the formation of these hydration products from the native proteïds present. Of the methods described, boiling after acidification to coagulate the native proteïds is the least trustworthy, as it leads to the formation of these proteolytic products. Devoto's modification of the ammonium sulphate method also is not free from this source of error. The methods which give good results are those in which either alcohol or trichloroacetic acid is used as the agent for coagulating the native proteïds. The trichloroacetic acid method possesses the advantage of being rapidly performed, although in the investigation of solid organs like the spleen, kidney, &c., the use of alcohol is preferable. The present experiments support previous conclusions that serous effusions (like the blood from which they originate) are free from proteoses and peptone. Gillespie's (this vol., ii, 81) conclusion to the contrary is due to his having employed untrustworthy methods.

W. D. H.

### **Elimination of Magnesium Compounds in cases of Rachitis.**

By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1895, 120, 1180—1181).—The proportion of magnesium compounds eliminated in the urine of children suffering from rachitis is very low. The urine contains a high proportion of various pigments which adhere very strongly to the precipitated salts obtained in the course of analysis, and offer considerable resistance to incineration.

C. H. B.

**Action of Distilled Water on Animal Organisms.** By F. S. LOCKE (*J. Physiol.*, 1895, 18, 319—331).—The poisonous action of distilled water on organisms has been again recently described by Ringer and Phear (this vol., ii, 239). In the present research the same animals, tadpoles and tubifex, were employed, and although the same results were obtained with ordinary distilled water, the inter-

pretation of these is different. Water distilled in glass has no such deleterious action, and the work of Nägeli points to traces of compounds of one or more of the heavy metals in distilled water allowed to come into contact with these. This he terms an "oligodynamic" property. Water distilled in glass becomes poisonous to life if placed in contact with a strip of metallic copper or brass. Metallic zinc is not so deleterious, and the results with lead were not quite so certain. This "oligodynamic" property can be neutralised by certain agencies, among which is the bringing of insoluble substances offering a large surface into contact with the water, or the dissolving of colloids in it. It is possible that the beneficial action of insoluble magnetic oxide of iron and tricalcium phosphate observed by Ringer and Phear is to be explained in this way, and possibly some of the crystalloid substances they employed similarly precipitate the noxious substance from the water.

W. D. H.

**Physiological Action of Toluylenediamine.** By WILLIAM HUNTER (*J. Pathol. and Bacteriol.*, 1895, 3, 259—294).—This contribution to the pathology of jaundice includes a review of previous work on the subject. The experiments recorded show that the concentration of the bile, so marked a feature of the action of the poison, is due to extensive catarrh of the bile ducts, extending from their origin downwards to the duodenum, occasioned by the excretion of the poison or its derivatives through the bile. This increase of catarrhal mucus finally arrests the flow of bile altogether. The inflammation in the duodenum itself is not regarded as essential. There is definite evidence that the drug appears in the bile an hour after its injection; by the fourth hour it is present in appreciable quantity; the special irritant action is, however, probably due rather to the derivatives of the drug. There are also changes in the blood of a destructive nature, the relationship of which to the jaundice is discussed at length.

W. D. H.

**Analysis of the Bone of a Mummy.** By THEZARD (*Compt. rend.*, 1895, 120, 1126—1128).—A very white, porous, and very brittle tibia of an adult human mummy from an Egyptian tomb of unknown age had the following composition:—Organic matter 24.031;  $P_2O_5$ , 24.700;  $CaO$ , 33.380;  $MgO$ , 0.762;  $K_2O$ , 0.126;  $Na_2O$ , 1.145;  $Fe_2O_3$ , 0.240;  $Al_2O_3$ , 0.534;  $SiO_2$ , 0.800;  $CO_2$ , 4.530;  $SO_3$ , 0.264;  $N_2O_5$ , 0.551;  $Cl$ , 0.709;  $F$ , traces; moisture, 7.900 = 99.672. The organic matter contained 3.163 of nitrogen, corresponding with 19.769 of proteids, 0.850 of fatty matter, and 3.412 of other organic substances, including a small quantity of a substance which gave the reactions for cellulose. Of the phosphoric anhydride, 2.644 was soluble in ammonium citrate, and 18.160 in acetic acid.

C. H. B.

**Phosphorus in Oysters.** By G. ADOLPHE CHATIN and ACHILLE MÜNTZ (*Compt. rend.*, 1895, 120, 1095—1097).—The authors have previously found (this vol., ii, 279) that the shells of oysters, and especially Portuguese oysters (*Gryphea angulata*), contain a considerable proportion of phosphorus. Further analyses give 0.038 per cent.



of phosphoric anhydride in the case of French oysters (*Ostrea edulis*) from Sables d'Olonne, and 0·089 per cent. in the case of Portuguese oysters from the beds at Oléron. Analyses of the two kinds of shells, which had been kept in the same bed for a year, gave 0·060 for the French and 0·118 for the Portuguese.

The bodies of the oysters themselves also contain considerable quantities of phosphorus, the proportion of phosphoric anhydride per 100 parts of dry organic matter being 1·836 in the case of the French and 2·052 in the case of the Portuguese oyster. Since the average weight of the flesh of the French oyster is 1·110 grams when dried, and of the Portuguese 1·157 grams, it follows that an average French oyster contains organic phosphorus equivalent to 0·020 gram of phosphoric anhydride, and the average Portuguese oyster, phosphorus equivalent to 0·032 gram.

C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Effect of Calcium and Magnesium on the Development of the Organised Structures of the Cell.** By THOMAS BOKORNY (*Ann. Agron.*, 1895, **21**, 350—352; from *Bot. Centr.*, **62**, 1) —Different algæ were kept for six weeks in nutritive solutions with and without calcium and magnesium, the solutions being contained in aluminium cups. The simultaneous absence of calcium and magnesium caused a diminution of the “chlorophyllean apparatus,” and also a great diminution or even disappearance of the nucleus; the absence of calcium alone caused a diminution of the chlorophyllean apparatus; whilst when magnesium alone was omitted the result was less decided, but there was a contraction of the nucleus. Loew’s theory that the chlorophyllean apparatus is a compound of calcium and nucleïn would explain the results obtained without calcium, and also the contraction of the nucleus.

Absence of potassium also gives rise to the diminution of chlorophyll bands, but that is due to the fact that without potassium there is no carbon assimilation; carbon assimilation and starch formation can take place in absence of calcium, which is only indirectly necessary to the function of chlorophyll.

N. H. J. M.

**Physiology of the Trichophytons.** By LESLIE ROBERTS (*J. Pathol. and Bacteriol.*, 1895, **3**, 300—309).—The examination of several varieties of fungus which occur in ringworm and allied conditions shows that their distinguishing feature is their ability to digest horny tissues, probably by means of a ferment. This *keratolytic* group includes *Favus*, the various kinds of *Trichophytons*, some *Aspergilli*, and probably others not yet identified. There are at least two natural distinctions observable in the purely trichophytic fungi, namely, a kind that digests both the cuticle and cortical substance of the hair simultaneously, and a variety that digests the cortical

substance, leaving the cuticle unaffected, or attacking it at a later period.  
W. D. H.

**Action of Calcium and Potassium Salts on the Herbage of Meadows.** By ÉMILE MER (*Ann. Agron.*, 1895, 21, 270—289).—The object of the author's experiments was the improvement of the peaty soils of the Vosges; his conclusions only apply to those soils. The pastures of the Upper Vosges, where the soil is a humous sand (containing 0·4 to 0·6 per cent. of nitrogen) are only benefited by the application of wood-ash (1200 kilos. per hectare), in very wet seasons; they require nitrogenous manure as well. In the case of peaty soils (nitrogen 0·6 to 1·2 per cent.), such an application of wood-ash is very effective, whilst without wood-ash they are sterile. Other peaty soils containing still more organic matter (nitrogen over 1·2 per cent.) require more wood-ash, and it may be preferable to burn the surface before applying the manure. The differences in the action of wood-ash seem to be due to the difference in the proportion of humus. It is suggested that nitrification may be more difficult in the soils containing less than 0·6 per cent. of nitrogen, and that such soils should receive an application of organic manure until they contain 0·8 to 1·0 per cent. of nitrogen, in order to make the calcium and potassium salts effective.

The applications of marl or soil which are considered necessary for peaty soils are expensive and unnecessary; all that is required is to neutralise the surface soil to the depth of a few centimetres, and to apply yearly the necessary manure. The peaty soils (with over 1·2 per cent. of nitrogen) and the marshes in France, hitherto considered useless, require to be investigated, on account of the large amount of humus they contain.  
N. H. J. M.

**Manuring Natural Meadows.** By ED. ZACHAREWICZ (*Ann. Agron.*, 1895, 21, 181—184).—In order to ascertain the best form of manure for meadow land, so as to obtain the greatest yield without injuring the quality of the herbage, an eight-year old meadow rich in nitrogen and moderately rich in potash and phosphoric acid, was divided into five parts and manured as follows. (1) Farmyard manure (20,000 kilos. per hectare); (2) complete artificial manure, (sodium nitrate 150 kilos., potassium chloride 150 kilos., superphosphate 500 kilos., and gypsum 400 kilos. per hectare); (3) superphosphate (500 kilos.) alone; (4) liquid manure; and (5) unmanured. There were three crops, giving the following total amounts. (1) 10,340, (2) 11,657, (3) 10,234, (4) 8,523, and (5) 8,081 kilos. Comparing the results obtained with the various manures and the cost of the manures with that of the unmanured plot, it is shown that the complete artificial manure was the most effective, superphosphate next, whilst with both farmyard and liquid manures there was less profit than with the unmanured plot.

N. H. J. M.

**Drainage from Cultivated Land.** By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1895, 21, 193—207; compare Abstr., 1894, ii, 291, and this vol., ii, 133).—Results obtained March, 1894, to March, 1895.—The rainfall

of the year was below the average, being high during the growing period, and low in the autumn and winter months. The amounts of nitric nitrogen in the drainage from the fallow cases was much less than was expected, and this can only be accounted for on the assumption that a large proportion of nitrates formed was taken up by cryptogamic vegetation. Stirring the soil gave a distinct increase of nitric nitrogen in the summer.

As regards the cases with vegetation, the yields of grass, beet, and wheat were not very high; there were excellent crops of oats in the cases manured with farmyard manure and sodium nitrate, an average yield of clover, and a good yield of sugar beet. There was most drainage from the grass case, very little with oats and clover. The vine case gave less drainage than the year before, but there was a distinct loss of nitrogen. The yield of sugar beet, on the land manured with farmyard manure, was comparatively low, but there was no loss of nitrates through drainage; whilst the cases manured with sodium nitrate gave larger crops, but lost a small amount of nitrate in drainage.

The loss of nitrates in drainage is inversely proportional to the amount of vegetation, and directly proportional to the amount of winter rain.

N H. J. M.

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## Analytical Chemistry.

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### Estimation of the Halogens in mixtures of their Silver Salts.

By FRANK A. GOOCH and CHARLOTTE FAIRBANKS (*Zeit. anorg. Chem.*, 1895, **9**, 349—355, also *Amer. J. Sci*, **50**, 27—32).—Treatment of the haloïd silver salts with mercuric cyanide, ammoniacal or acid cuprous chloride, potassium ferrous oxalate, chromous chloride, chromous acetate, or magnesium powder and dilute acids, gave results of no analytical value. A mixture of hydrogen sulphide and ammonium sulphide vapour at 200° completely decomposes silver chloride, but the bromide and iodide only partially, and the reaction is not completed even at much higher temperatures. Good results, as the analyses show, are obtained by modifying Kinnicut's electrolytic method. The mixed silver chloride and bromide is collected on an asbestos filter, which is fitted with a platinum sieve above the asbestos, washed, dried, weighed, and cautiously fused; the electrolysis is conducted in presence of alcoholic oxalic acid solution (25 per cent. alcohol 1 part, oxalic acid 0·1 part). If iodide is present, the method must be modified by employing as solution a mixture of 40 per cent. acetic acid (2 vols.) neutralised with ammonia, to which is added ammonia (1 vol.), aldehyde of 75 per cent. (1 vol.), and alcohol (1 vol.); any ammonium iodate which may be deposited on the anode is readily removed by dipping it into hot water. The analyses occupy about 7 hours; the current = 0·5—0·25 ampere. The use of sulphuric acid for the electrolysis is objectionable, as its removal from the spongy silver is extremely difficult. J. B. T.

**Estimation of Fluorine.** By PAUL JANNASCH and A. RÖTTGEN (*Zeit. anorg. Chem.*, 1895, 9, 267—273).—The method consists in distilling off the fluorine as hydrogen fluoride in an apparatus made entirely of platinum; the distillation flask being arranged so that air and carbonic anhydride can be passed through it. Sodium fluoride is introduced into this flask, and then sulphuric acid, and the mixture heated in a bath of phosphoric acid at 155—160°, a brisk current of air and a slow current of carbonic anhydride being passed through the flask at the same time. The hydrogen fluoride is carried over with the gases and, by means of an inverted funnel, is passed into a solution of pure sodium hydroxide contained in a platinum dish. When all the hydrogen fluoride is expelled, which takes about 4—6 hours, the apparatus is allowed to cool with the current of gases passing through it. The soda solution containing the fluorine is precipitated with a hot 25 per cent. calcium chloride solution, and the precipitate after being washed and ignited, is treated with the theoretical quantity of dilute acetic acid for dissolving the calcium carbonate; a slight excess of acetic acid is then added and the solution evaporated to dryness on the water-bath and heated until the odour of acetic acid has disappeared. The dry residue is treated with hot water, and the insoluble calcium fluoride collected, washed, and ignited in a platinum crucible. The results are accurate and agree with those obtained by the ordinary methods.

The authors are engaged in the application of this method to the analysis of cryolite, fluor spar, and silicates. E. C. R.

**Precipitation and Gravimetric Estimation of Carbonic Anhydride.**—By FRANK A. GOOCH and I. K. PHELPS (*Zeit. anorg. Chem.*, 1895, 9, 356—359; also *Amer. J. Sci.*, 50, 101—103).—The weighed carbonate is placed in a flask of about 50 c.c. capacity; boiled water (20—30 c.c.) is added, and a small test-tube containing hydrochloric acid. This flask is connected with the longer limb of a bent tube in which a bulb is blown just above the neck of the flask; to the shorter limb a tube is attached, passing through the cork of the absorption cylinder to the bottom and having a valve at the lower end; the absorption cylinder consists of a wide glass tube to the bottom of which is fastened a rubber balloon, the top being closed by a doubly bored rubber cork, a short tube with a stopcock is fitted in the one opening whilst through the other passes the tube from the evolution flask. The carbonic anhydride is absorbed by means of barium hydroxide solution (5 per cent.). When the evolution of carbonic anhydride from the flask ceases, the liquid is heated until the barium hydroxide solution almost boils, the latter is then decanted through a filter moistened with water and xylene (5 c.c.), the carbonate thoroughly washed with hot water, and finally once with alcohol. The barium carbonate on the filter and in the absorption tube is dissolved in hydrochloric acid, and precipitated with sulphuric acid. The operations are quickly performed, and the results are extremely accurate. J. B. T.

**Estimation of Selenious acid by means of Potassium Permanganate.** By FRANK A. GOOCH and C. F. CLEMONS (*Zeit. anorg. Chem.*, 1895, **9**, 360—364; also *Amer. J. Sci.*, **50**, 51—54).—Selenious acid readily decolorises potassium permanganate solution; but, in presence of sulphuric acid, secondary actions are apt to vitiate the analytical results. This difficulty has been successfully overcome by limiting the quantity of sulphuric acid, and oxidising at a comparatively low temperature.

Selenious anhydride is dissolved in dilute sulphuric acid (5 per cent. by vol.), and potassium permanganate solution (N/10) added in excess; the liquid is then rendered colourless by the addition of a known quantity of normal oxalic acid solution, and the excess of this is determined with permanganate, in the usual manner, at a temperature not exceeding 50—60°. J. B. T.

**Estimation of the Manurial Value of Phosphates.** By G. PATUREL (*Ann. Agron.*, 1895, **21**, 325—342; compare this vol., ii, 28).—The following method is recommended as giving results in accordance with ideas established by actual vegetation experiments. The powdered phosphate (1 gram) is treated with 500 c.c. of water containing crystallised citric acid (5 grams). The mixture is frequently shaken for 24 hours, filtered, and the phosphoric acid determined. The total phosphoric acid is also determined, and the relation of the soluble to total phosphates calculated. Basic slags are treated gradually with the citric acid solution, so as to dissolve most of the calcium carbonate before attacking the phosphate. N. H. J. M.

**Use of Perchloric acid in the Estimation of Potassium.** By D. ALBERT KREIDER (*Zeit. anorg. Chem.*, 1895, **9**, 342—348).—See this vol., ii, 444.

**Analytical Characters of a Mixture of Salts of Barium, Strontium, and Calcium.** By HENRI BAUBIGNY (*Bull. Soc. Chim.*, 1895, [3], **13**, 326—330).—The metals in question having been precipitated as carbonates in the usual manner, are redissolved in hydrochloric acid, taking care to avoid excess; the barium is then precipitated as chromate in acetic acid solution, and the strontium as sulphate by means of dilute potassium sulphate (0.25 per cent.). The calcium is reprecipitated with potassium carbonate to eliminate the chromate, and the solution of its chloride, from which free hydrochloric acid has been removed by the addition of ammonium acetate, is precipitated by potassium ferrocyanide in presence of a large excess of ammonium chloride. The residual strontium is not precipitated under these conditions, but the method is not available for its separation, as it is liable to be carried down with the potassium calcium ferrocyanide.

When it is required to test for calcium only, the barium and strontium may be removed by means of a concentrated solution of potassium sulphate.

A modification of the first plan, in which the elimination of the

chromate is avoided, is based on the reduction of the free chromic acid by the ferrocyanide. The barium having been removed as chromate, the strontium, if present, is entirely precipitated by a saturated solution of potassium sulphate; the filtrate is then saturated with ammonium chloride, and the calcium precipitated by excess of ferrocyanide.

In the case of extremely dilute solutions, such as might remain after the precipitation of the metals as carbonates in presence of a very large excess of ammonium chloride, the barium may be entirely precipitated with normal chromate, and the strontium recognised by the addition of a drop of sulphuric acid to the filtrate. The calcium is then detected by the addition of potassium ferrocyanide to a fresh portion of the original solution saturated with ammonium chloride.

JN. W.

### Separation of Metals in a Current of Hydrogen Chloride.

By PAUL JANNASCH and F. SCHMITT (*Zeit. anorg. Chem.*, 1895, 9, 274—282).—*Separation of Arsenic and Lead.*—The general method employed has been already described (this vol., ii, 89). The mixture of lead nitrate and arsenious acid is dissolved in nitric acid, the excess of acid carefully evaporated in a special glass vessel at 120° by means of a current of dry air, the residue being gradually heated to 200° in a current of dry hydrogen chloride. The arsenic, which is converted into arsenic chloride, distils over, and is collected in a 10 per cent. solution of nitric acid, which is evaporated on the water bath with concentrated nitric acid. The residue is dissolved in water and precipitated with a solution of magnesium chloride (*J. pr. Chem.*, 45, 99). The residue of lead chloride remaining in the distillation apparatus is tested for arsenic, and is then either weighed as such or is dissolved in hydrochloric acid and the lead estimated by one of the ordinary methods.

*Separation of Arsenic and Copper.*—This is effected in a similar way to the preceding. The separation is not, however, complete when the distillation is carried out at 200—250°, but it is complete after heating for two hours at 300°. The residue of copper chloride is evaporated to dryness with concentrated nitric acid, carefully dried in an air bath, and finally cautiously heated over a bare flame and weighed.

*Separation of Arsenic and Iron.*—This is complete on heating at 110—120° during 1½ hours. After the distillation, the iron remains as beautiful, brownish-green scales of the chloride, which dissolve completely in water. The solution is heated with a small quantity of nitric acid, and the iron precipitated with ammonia.

Arsenic and tin cannot be separated by this method, for the chlorides of both volatilise easily at 120°.

*Separation of Tin and Lead.*—The mixture of tin foil and lead nitrate is dissolved in aqua regia and the salts dried in a current of air, as previously described. The distillation in hydrogen chloride is effected at 200°, and is complete in about a quarter of an hour; the distillate of tin chloride, after adding ammonia in excess, and then ammonium sulphide, is acidified with hydrochloric acid, and the precipitate of tin sulphide collected, washed with a solution containing ammonium



nitrate and hydrogen sulphide, and dried at  $90^{\circ}$ . It is then heated in the air as long as sulphurous anhydride is evolved, and finally at a higher temperature in a current of oxygen until the weight is constant.

The separation of tin and copper is effected in a similar way, and is complete after two hours at  $250$ – $300^{\circ}$ . The residue contains both cupric and cuprous chlorides, the latter being formed by the elimination of chlorine from cupric chloride at the high temperature employed and in presence of hydrogen chloride.

Tin and iron are separated in a similar manner. The separation is complete after one hour at  $120^{\circ}$ .  
E. C. R.

**Detection and Estimation of Metals in Fatty Oils.** By HEINRICH FRESENIUS and A. SCHATTENFROH (*Zeit. anal. Chem.*, 1895, **34**, 381–390).—The experiments were made on oleates of the metals (lead, iron, zinc, aluminium), or in the case of copper, verdigris, dissolved in oil of sesame. With the exception of lead, all the metals could be estimated by simple incineration of the oil. Shaking the oil with dilute nitric acid in all cases extracts the whole of the metal. In the case of lead, the oil can be dissolved in ether and shaken with dilute sulphuric acid, when the whole of the lead separates as sulphate. Zinc is better extracted with hydrochloric acid; the acid solution is then evaporated with excess of mercuric oxide and the residue ignited, when the zinc is left as oxide.  
M. J. S.

**Estimation of Formic acid by Potassium Permanganate.** By HARRY C. JONES (*Amer. Chem. J.*, 1895, **17**, 539–541; compare Lieben, *Abstr.*, 1894, ii, 219).—This is best effected by making the solution alkaline with sodium carbonate, warming, and treating it with a known excess of standard permanganate solution; the solution is then acidified with sulphuric acid, a measured excess of oxalic acid is run in, so as to destroy the permanganate and bring the precipitated manganese oxide into solution, and then the excess of oxalic acid is estimated by titration with the original permanganate solution; the permanganate equivalent of the solution of oxalic acid used being known, the difference between this and the total amount of permanganate used in the first experiment is the permanganate equivalent of the formic acid present.

It is not possible to determine oxalic acid in the presence of formic acid by titration with permanganate if the solution is acidified with sulphuric acid, as a portion of the formic acid is also oxidised under the circumstances.  
C. F. B.

**Analysis of Must and Wine.** By A. HALENKE and W. MÖSLINGER (*Zeit. anal. Chem.*, 1895, **34**, 263–293).—The authors lay stress on the importance of a more frequent and complete analysis of grape must than has been usual, and the necessity of employing standard methods. They here publish the results of the examination of 116 samples of must, obtained in 1892 from various localities in the Rhine-Palatinate, in which they have estimated the specific gravity, the alcohol, the dextrose and levulose, the tartaric acid, both free and as metal hydrogen tartrate, the malic acid, ash, phosphoric

acid, total dry residue, and (by difference) the neutral non-saccharine constituents. The results are expressed in grams per 100 c.c.

The sample must be made perfectly clear by filtration, and owing to the rapid alterability of the must, all the determinations must proceed as nearly as possible simultaneously and without interruption. The sp. gr. (which they express in terms of Oechsle's degrees) must be determined by weighing, and not by the hydrometer. For the alcohol estimation, a table by Windisch gives at once grams per 100 c.c. The polarisation and copper reduction should be carried out on the same portion to eliminate small errors; the Landolt-Lippich polarimeter is recommended; and the copper reduction is performed according to Meissl's method, whose tables for obtaining the results in inverted sugar are also used. Applying the values given by Tollens, von Gubbe, and von Ost, for the specific rotation of the sugars, the formulæ for calculating the dextrose ( $d$ ) and levulose ( $l$ ) are  $l = \frac{0.525s + a}{1.48}$  and  $d = s - l$ , where  $a$  is the lævo-rotation, and  $s$  the total

sugar per 100 c.c. In nearly all the samples examined, the amount of levulose exceeded that of dextrose. In estimating the total dry residue, the application of heat is inadmissible. The only satisfactory method is to mix the weighed must (1 gram or less) with 10 grams of sand, and dry in a vacuum over sulphuric acid; 100—150 hours are required. The solids can, however, be calculated very closely from the sp. gr. of the aqueous residue of the alcohol distillation; 1° Oechsle corresponds with 0.2636 gram of dry residue per 100 c.c. For the total acidity, the wine should be heated just to the boiling point, as this expels carbonic anhydride and renders the end-reaction very sharp. The indicator is a bluish-violet litmus paper, prepared by dissolving 0.2 gram of azolitmic acid in 250 c.c. of boiling water, adding 1.25 c.c. of normal potash, soaking strips of filter paper (Schleicher and Schull's 595), and drying the strips in the dark. The point at which the wine ceases to redden the test paper is taken as the end of the titration. For estimating the total tartaric acid, the methods of Berthelot-Fleurieu, Nessler-Barth, and Haas leave much to be desired. The authors prefer to make use of the very sparing solubility of potassium hydrogen tartrate in a 10 per cent. solution of potassium chloride (see Grosjean, *Trans.*, 1879, 348). To 100 c.c. of the must are added 2 c.c. of glacial acetic acid, and 15 grams of powdered potassium chloride, and, when this is, as far as possible, dissolved, 20 c.c. of alcohol. After a few minutes' stirring and 15 hours' repose, the precipitate is collected on a Gooch filter, using a filter-bed of paper fibre. After washing several times with a solution of 15 grams of potassium chloride in 100 c.c. of water and 20 c.c. of alcohol, and then with strong alcohol alone, the acidity of the precipitate is titrated, and a correction of 0.15 c.c. of normal alkali is made for the potassium hydrogen tartrate not precipitated. In applying this method to must, it is necessary to precipitate a second time, as it is found that other acid substances, of unknown nature, are simultaneously precipitated the first time. The tartaric acid existing as potassium hydrogen tartrate is best found from a comparison of the alkalinity of the ash of the must with the total tartaric acid found.

The preparation of the ash requires much care. The residue must be slowly charred in a covered platinum basin without visible combustion until it yields a colourless aqueous extract, then exhausted with boiling water, and the residue very slowly burnt to a white ash. The entire ash is rendered acid with a measured quantity of  $N/2$  acid, and the excess of acid titrated, or the potassium and calcium may be estimated apart by making separate titrations of the total aqueous extract of the ash, and of the residue insoluble in water. The malic acid is deduced from the difference between the total tartaric acid and the total acidity.

M. J. S.

**Analyses of Austro-Hungarian Sweet Wines.** By LEONHARD ROESLER (*Zeit. anal. Chem.*, 1895, **34**, 354—361).—These wines are prepared by extracting dried grapes with a good ordinary wine and fermenting the extract. They contain usually 10—15 volumes per cent. of alcohol, 0.55—1.2 grams of phosphoric acid, 2—5.5 grams of total ash, 100—250 grams of sugar (inverted), 26—45 grams of extractive matters other than sugar, 5—10 grams of glycerol, and 5—10 grams of total free acid per litre. Tokay is, on the average, slightly more alcoholic, contains rather less ash (seldom reaching 4 grams per litre), about the same amount of non-saccharine extractive matters, but invariably more than 10 grams of glycerol, and usually above 15 grams, per litre.

M. J. S.

**Examination of Decomposed Human Remains for Alkaloids and Glucosides.** By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1895, **34**, 294—346).—The well-known difficulty of distinguishing, in chemico-legal cases, the ptomaines from the poisonous vegetable alkaloids, has led to numerous proposals for modifications of the recognised methods for the extraction and identification of the latter. The author confirms this difficulty by showing that extracts of putrefied human remains, whether made with acid or alkaline liquids, whether aqueous or alcoholic, all contain substances which give precipitates with the ordinary reagents for the vegetable alkaloids. Both classes of alkaloids, together with the peptone and albumin occurring in cadaveric extracts, are precipitated by tannin, but, on treating the moist precipitate with water containing glycerol, the tannates of the vegetable alkaloids are all dissolved, whilst the cadaveric products liable to be confounded with them are left in the insoluble residue. Dry glycerol and tannin, when heated together, unite, with elimination of water, forming a compound which the author names "glycerotannic acid;" its solvent power was demonstrated for 34 of the commoner alkaloids and glucosides.

The process of extraction is as follows. The cadaveric matter is digested at  $40^{\circ}$  for two days—with or without addition of water—with glycerol, in which abundance of tannin has been dissolved; the liquid is then separated from the solid matter by pressing, and, after heating to  $50^{\circ}$  to coagulate blood fibrin and traces of albumin, is cooled and filtered. It is then shaken with light petroleum to remove fat, and the last traces of petroleum are removed from the aqueous

liquid by warming on the water bath; the alkaloids are then extracted in two portions by shaking with chloroform, first in presence of acid, and, secondly, after making alkaline with potash. Chloroform is much to be preferred to the ether of the Stas-Otto process, since it removes with quantitative completeness many alkaloids which are with difficulty extracted by ether. The exceptions are morphine, narceine, curarine, and strophantin. The two first can be extracted by a mixture of chloroform and alcohol, after the alkali hydroxide has been converted into carbonate by adding sodium or potassium hydrogen carbonate, and the last can be removed by ether-chloroform (equal volumes), preferably after saturating the solution with sodium chloride. If metallic poisons have to be looked for, the original extraction should be made with acidified alcohol, and the glycerotannic acid treatment applied only to the aqueous solution of the residue left after evaporating the alcohol. In either case, the alkaloids are left on evaporating the chloroform solution.

*Separation of the Alkaloids from one another.*—In this section a mass of detail is given, of which the following is a rough outline.

Class 1. *Alkaloids, &c., Extracted by Chloroform from Acid Solution.*

—Colchicine, digitalin, papaverine, narcotine, delphinine, aconitine, agaricin (all precipitated by tannin solution which has been acidified with hydrochloric acid almost to the point of becoming turbid); picrotoxin, and cantharidin (not precipitated by acidified tannin). Of these, cantharidin, picrotoxin, agaricin, colchicine, and digitalin are precipitated by potash; whilst delphinine, aconitine, narcotine, and papaverine are not so precipitated. Aconitine, whose picrate is insoluble in ammonia, can be separated by this means from narcotine and papaverine, whose picrates are soluble; and narcotine is separable from papaverine by the solubility of its acid oxalate in cold alcohol.

Class 2. *Alkaloids Extracted by Chloroform from Alkaline Solution.*

—Brucine, strychnine, emetine, veratrine, narcotine, codeine, thebaine (all precipitated by acidified tannin solution); atropine, sparteine, and nicotine (not precipitated by acidified tannin). Nicotine, conine, and sparteine can be distilled over with steam and thus separated from atropine. Strychnine may be separated from brucine by adding a small excess of potassium ferrocyanide, filtering after 15 minutes, and rapidly washing, then treating with ammonia, and extracting with chloroform; brucine from veratrine, codeine, and emetine by taking advantage of the difference in the solubilities of their chromates in water feebly acidified with acetic acid; brucine from thebaine by the insolubility of its dichromate in hydrochloric acid; brucine from veratrine and thebaine by treating the alcoholic solution with alcoholic mercuric chloride. Thebaine picrate is insoluble in acetic acid; the picrates of codeine and strychnine are soluble.

Class 3. *Alkaloids, &c., not Extracted from Solution by Chloroform.*

—Narceine and strophantin are precipitated by acidified tannin solution; morphine not. Also morphine may be separated from narceine by mixing with a large quantity of ammonium chloride and adding N/20 iodine solution. The narceine alone is precipitated as per-

iodide (see below), and the excess of iodine is titrated in the filtrate.

*Volumetric Estimation of the Individual Alkaloids.*—After weighing the residue from the chloroform solution, it must be titrated to ascertain whether it consists entirely of the alkaloid in question. Veratrine, narcotine, atropine, codeïne, papaverine, thebaine, strychnine, and narceïne (all in hydrochloric acid solutions), and morphine (in neutral solution) can be titrated with iodine. A measured volume of the dilute alkaloid solution is placed in a small stoppered flask, a small excess of N/20 solution of iodine in potassium iodide is added, and the mixture left in repose from 5 to 25 minutes, or until the supernatant liquid begins to clarify. The reaction is in no case completed instantly. The liquid is then filtered through glass-wool and asbestos into a clean, dry, stopcock burette, and the excess of iodine in a measured portion is titrated with thiosulphate and starch. In all cases, 1 mol. of the alkaloid precipitates 3 atoms of iodine, and the author gives for the precipitates the general formula  $\text{Alk, HI, I}_2$ , and assumes that the HI of the formula is derived from a reaction of iodine with water in which hydrogen peroxide is produced.

Mayer's reagent (potassio-mercuric iodide) can be employed for the titration of most of the alkaloids. The end of the precipitation is ascertained by placing a drop of the liquid upon the upper of two superposed filters, and testing the moistened spot on the lower filter with ammonium sulphide.

Brucine (which cannot be titrated by iodine), strychnine, codeïne, and thebaine, can be very well titrated by mercuric chloride alone, testing as above, but stirring and rubbing for some time with the glass rod before taking the drop for testing. The presence of a mineral acid is not objectionable, but acetic acid and alcohol must be avoided.

In conclusion, three test analyses are given, in which the above methods were applied with excellent results to the recovery of weighed amounts of narcotine and codeïne, strychnine and veratrine, morphine and narceïne respectively from putrefied human remains.

M. J. S.

**The Phosphomolybdic acid Test in Lard Analysis.** By GEORGE F. TENNILLE (*J. Amer. Chem. Soc.*, 1895, ii, 33—41).—The author has investigated this test which has been strongly recommended for the detection of vegetable oil in lard. The result is that the test does not work unless the amount of oil exceeds 10—15 per cent., but such large additions are more safely detected by other methods. The test is, therefore, but of slight analytical value. L. DE K.

**Tests for Distinguishing Atropine from Strychnine.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1894, ii, 816; from *Boll. Chim. Farm.*, 33, 449) —Atropine when evaporated with nitric acid develops the odour of hawthorn; strychnine remains odourless; moreover, the residue with strychnine is yellow, whilst that of atropine is colourless. When the atropine residue is moistened with alcoholic potash and evapo-

rated, a violet residue is obtained; strychnine gives a yellow coloration, passing into reddish-violet on further addition of potash. Addition of water to the alcoholic potash mixture renders the atropine colourless; strychnine turns yellow. The atropine residue, with ammonia, yields little yellow drops which change to violet on adding alcoholic potash; strychnine under these circumstances gives with ammonia a reddish-orange coloration, and then, on adding alcoholic potash, a transitory violet coloration which passes into blood-red. If this ammoniacal solution is agitated with chloroform, and the latter evaporated, the atropine residue is nearly colourless, but turns permanently violet on addition of alcoholic potash; the strychnine residue is yellow, and turns reddish-orange with alcoholic potash.

L. DE K.

**Estimation of Indigotin.** By JOSEF SCHNEIDER (*Zeit. anal. Chem.*, 1895, **34**, 347—354).—All the methods hitherto published are wanting in accuracy. The use of pure naphthalene as a solvent presents many advantages, and the apparatus is arranged as follows. A 300 c.c. conical flask is provided with a condenser, which has an entrance at the side of the tube, but has its lower end drawn out to a point and bent sideways. This delivers the condensed naphthalene into a cartridge-shaped filter (Schleicher's extraction thimbles would serve well if made of smaller dimensions), suspended by a thread inside the flask; in this filter is placed 0.5 to 1 gram of the indigo, mixed with glass-wool, and the flask, supported on double wire gauze, is heated with a flame. Fifty grams of naphthalene, which must be free from ash, is used, and the cobobation is continued for a short time after the filtrate ceases to be coloured, about  $5\frac{1}{2}$  hours being required. The indigotin is then precipitated (as in Stein's process) by adding to the naphthalene solution 150 c.c. of ether (which should be free from alcohol), collecting the precipitated indigotin on a weighed filter, washing with ether, and drying at  $100^{\circ}$ . It is well to weigh with the empty filter a separate piece of paper, by which the last traces of indigotin can be wiped out from the flask. The loss of indigotin from decomposition, volatilisation, and imperfect precipitation amounts to 1—4 milligrams. Perfect dryness of the apparatus and materials is necessary in order to avoid explosions.

M. J. S.

**Estimation of Peptones.** By DUTTO (*Chem. Centr.*, 1894, ii, 1022; from *Pharm. Centr. Halle*, **35**, 636).—The solution of the peptones is precipitated with potassium bismuth iodide, and the precipitate, after being washed with water very slightly acidified with sulphuric acid, is dried in a vacuum. The bismuth contained in it is now estimated as  $\text{Bi}_2\text{O}_3$ . One gram of peptone corresponds with 0.141—0.147 gram of metallic bismuth.

L. DE K.

## General and Physical Chemistry.

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**Possible Explanation of the two-fold Spectra of Oxygen and Nitrogen.** By EDWARD C. C. BALY (*Proc. Roy. Soc.*, 1895, 57, 468—469).—Experiments have been undertaken to determine if the two spectra of oxygen are produced by two distinct gases resulting from a dissociation of oxygen, a combination of the two being what is usually called oxygen.

Oxygen was sparked in an apparatus similar to that used by J. J. Thomson in his experiments on the electrolysis of steam. In the first experiments, the distance between the electrodes was 35 mm., and the highest pressure compatible with the appearance of the two spectra was made the starting point of the experiments. The fractions obtained from the anode and cathode were weighed. They follow the lines of Thomson's results, inasmuch as with long sparks a lighter fraction was obtained at the cathode, and with short sparks a heavier fraction. The fractions from the anode were not so definite as from the cathode, although the difference was in the right direction. The density of the cathode fraction with long sparks varied from 15·78 to 15·80, with short sparks from 16·00 to 16·06; the density of the unsparked oxygen from 15·87 to 15·89. The density of the cathode fraction from oxygen, previously for three days fractionated with short sparks, was 15·75. E. C. R.

**Fluorescence of Argon and its Combination with the Elements of Benzene.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 1386—1390).—The combination of argon with benzene vapour under the influence of the silent electric discharge (this vol., i, 412, and ii, 337) takes place slowly, and is influenced by the presence of mercury vapour, which intervenes in the form of a volatile compound. The luminescence, which is at first violet and visible only in the dark, becomes green after about an hour, and shows lines at 579, 577, 546, and a band at 516·5. A photograph of the spectrum shows the principal bands of nitrogen, and feebler lines at 436, 405, and 354. As the discharge continues, the intensity of the luminescence as a whole and of the lines 579, 577, and 546 steadily increases, but that of the band 516·5 diminishes. After seven hours, the nitrogen bands disappear, probably because all the nitrogen has combined with the benzene. After eight hours more, the luminescence has a brilliant emerald-green colour, and is visible in full daylight. A photograph of the spectrum shows the lines 579, 577 and 546, 436, 405, 354, 313, 312, two faint lines at 420 and 416, and the lines 385 and 358, and this spectrum persists during 30 hours of uninterrupted discharge.

The band 516·5 is due to hydrocarbons at low pressure, and the lines 313 and 312 are due to mercury vapour at low pressure. The other lines seem to coincide with lines observed by Crookes in argon under low pressure. As already pointed out (*loc. cit.*), none of the

lines coincide with the helium line nor with the principal line of the aurora borealis 557. The strong argon line at 555.7 is, however, somewhat near the latter, and it seems probable that there is some relation between the presence of argon in the atmosphere and the production of the aurora borealis.

It is particularly noteworthy that many of the lines observed by Crookes in the argon spectrum, and many of those shown by the green luminescence, coincide with lines of mercury vapour under low pressure, for instance, the lines at 579, 577, 546, 436, 405, 354. The lines at 420, 416, 385, and 358 seem to belong to argon alone, and the lines 313 and 312 to mercury alone. No known gas shows these lines and the green luminescence when subjected to the silent discharge; they are not shown by argon in presence of mercury vapour at the normal pressure, nor by nitrogen in presence of benzene vapour or carbon bisulphide and mercury, and with argon in presence of benzene or carbon bisulphide and mercury they are not seen until after the discharge has acted for some time. They appear only after the benzene has been partially converted into condensation products. One of these products at the moment of its formation begins to unite with both argon and mercury, the two being associated probably because they both have monatomic molecules.

The green luminescence persists even after all the benzene seems to have disappeared, but it ceases after very prolonged action of the discharge, probably because the whole of the benzene has been altered. When once the green luminescence is well established, the compounds which cause it are stable, and if the discharge be interrupted, even for several hours, and is started again, the luminescence appears almost immediately with its former intensity. Neither the product of condensation alone nor the residual gas alone shows the phenomenon, and a mixture of fresh argon with the product of condensation shows the characteristic tint and lines after the discharge has acted on it for a long time. The addition of a trace of benzene to the mixture materially shortens the time required, but an excess of benzene increases it.

C. H. B.

**New Gas obtained from Uraninite.** By J. NORMAN LOCKYER (*Proc. Roy. Soc.*, 1895, **58**, 67—70, 113—119, 192—195).—An account of the spectroscopic results obtained with the gases extracted from uraninite and other minerals by heating in a vacuum. A table is given comparing the lines photographed between  $\lambda$  3889 and 4580, with chromospheric lines, eclipse lines (1893), and some stellar lines (compare this vol., ii, 431).

H. C.

**Direct Spectrum Analysis of Minerals and Fused Salts.** By ARNAUD DE GRAMONT (*Compt. rend.*, 1895, **121**, 121—123).—Many minerals have sufficient conductivity or volatility to permit the passage of a condensed electric spark between two small fragments of the mineral attached to the poles of the coil. With a condensed spark, the spectrum shows the lines both of the metals and of the non-metals present in the mineral; without the condenser, the spectra



of the non-metals disappear, and those of the metals show only the brightest lines.

Certain fused salts behave in a similar way, and when the condensed spark is used, the spectrum contains the lines of all the elements present, together with some air lines, which, however, are much enfeebled, especially if the striking distance is short. Without the condenser, the spectra are complex and characteristic of each particular salt; probably they are produced by undissociated molecules.

In the case of minerals, the use of the condensed spark gives the best results, but, in the case of salts, the spark without a condenser often gives valuable indications.

If the electrodes are coated with sulphur, arsenic, or selenium, a condensed spark gives the line spectrum of the element, and the latter does not burn; an uncondensed spark, on the other hand, causes the non-metals to ignite.

C. H. B.

**Absorption Spectra of Dilute Solutions.** By THOMAS EWAN (*Proc. Roy. Soc.*, 1895, **57**, 117—161).—Experimental details of a paper previously published in an abridged form (this vol., ii, 433).

**Refraction and Dispersion of Liquid Oxygen, and the Absorption of Liquid Air.** By GEORGE D. LIVEING and JAMES DEWAR (*Phil. Mag.*, 1895, **40**, 268—272).—The refraction was determined by the method previously employed (*Abstr.* 1894, ii, 37), but with a vacuum-jacketed globe in place of the cylindrical tube. The values so obtained were  $\lambda$  4416 (blue cadmium),  $\mu = 1.2249$ ;  $\lambda$  6438 (red cadmium),  $\mu = 1.2211$ ;  $\lambda$  5350 (green thallium),  $\mu = 1.2219$ ;  $\lambda$  6705 (red lithium),  $\mu = 1.2210$ ;  $\lambda$  5892 (D sodium),  $\mu = 1.2219$ . The value for the D line is considerably less than that previously obtained. The refraction constants for the mean green are hence 0.1242 (Lorenz) and 0.1953 (Gladstone), the similar values for gaseous oxygen being 0.12631 and 0.18947.

Cauchy's coefficient of dispersion is calculated, and found to be 0.0064, a number agreeing with the mean value of Mascart's determinations for the gaseous element. The absorption spectrum of liquid air was also examined, and the absorption bands observed to be better developed by pure oxygen than by five times the thickness of air, Janssen's law being apparently obeyed. The bands also were sensibly widened and strengthened by the reduction of the temperature.

L. M. J.

**Active Alkyls of the  $\alpha$ -Hydroxybutyric acids.** By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1895, **120**, 1274—1276).

	[ $\alpha$ ] <sub>D</sub> .
I. Butylic acetylhydroxybutyrate . . . . .	—27.9
Isobutylic                   "                   . . . . .	—30.7
Heptylic                    "                   . . . . .	—21.8
Octylic                     "                   . . . . .	—18.6

	[ $\alpha$ ] <sub>D</sub> .	Corrected.
I. Isobutylic acetylhydroxybutyrate. ....	+27.9	+27.9
" propionylhydroxybutyrate..	+20.5	+27.7
" butyrylhydroxybutyrate ...	+18.0	+24.4
" valerylhydroxybutyrate....	+13.9	+18.7
" caproylhydroxybutyrate ...	+12.1	+16.1
" nonanoylhydroxybutyrate..	+ 9.0	+12.1
" benzoylhydroxybutyrate ...	— 0.89	— 1.2
III. Isobutylic $\alpha$ -chlorobutyrate .....	—10.5	
" $\alpha$ -bromobutyrate .....	+ 8.2	
" nitroisobutyrate .....	—43.2	

IV. *Condensation Products with Aldehydes* (this vol., i, 332).—

	[ $\alpha$ ] <sub>D</sub> .
Methylene derivative of lævogyrate acid.....	—5.9
Racemic valeraldehyde and dextrogyrate acid..	+6.5
Dextrogyrate valeraldehyde and dextrogyrate acid .....	+8.4

V. *Amylic Valerylhydroxybutyrates*, obtained by the action of valeric chloride on amylic hydroxybutyrates :—

(a.) Racemic acid, racemic alcohol, active chloride ..	+ 0.1
(b.)     "           active           "           racemic chloride..	+ 0.6
(c.) Active acid, racemic alcohol, racemic chloride ..	—15.3
(d.)     "           active           "           active           " ..	—15.1

On the assumption of a regular tetrahedron with the masses at the four solid angles, the compounds in Series I should be dextrogyrate; the compounds in Series II should be lævogyrate up to the butyryl derivative, and dextrogyrate from the caproyl derivative. The corrected values in Series II are obtained by multiplying the observed values by 1.35, the ratio between the dextrogyrate and lævogyrate isobutylic hydroxybutyrates. It is obvious that the simplified formula for the product of asymmetry is not sufficient in the majority of these cases.

In Series V, there is evidence of the superposition of the optical effects of three asymmetric carbon atoms; according to the rules already established (this vol., i, 149 and 195), the algebraic sum of the rotatory powers of the compounds (a), (b), and (c) should be equal to the rotatory power of the compound (d). C. H. B.

**Optical Activity of Amylic Derivatives in the state of Liquid and of Vapour.** PHILIPPE A. GUYE and A. P. DO AMARAL (*Compt. rend.*, 1895, 120, 1345—1348).—The following results show that, except in the case of amylamine, the rotatory power of liquid amylic compounds diminishes with a rise of temperature.

Measurements of the rotatory powers of some of these compounds in the form of vapour, by methods which will be described subsequently, show that in the case of amylic acetate, amylic chloracetate, diamyl, and amylamine, the differences between the rotatory powers

	<i>t.</i>	$[\alpha]_D$	<i>t.</i>	$[\alpha]_D$
Valeraldehyde.....	13·0°	+14·09	72·5°	+11·14
Valeraldoxime .....	20·0	+11·13	50·9	+ 9·97
Amylic acetate .....	18·0	+ 2·54	57·6	+ 2·51
Methylic valerate.....	18·0	+14·63	—	—
Amylic chloracetate...	26·8	+ 3·00	51·3	+ 2·97
Diamyl.....	19·9	+10·01	—	—
Isobutylamyl.....	21·0	+ 5·31	65·2	+ 5·20
Amylamine.....	20·0	— 1·58	67·1	— 1·67
Diamylamine .....	18·0	+ 5·59	57·9	+ 4·71
Amylic bromide .. ..	18·0	+ 2·51	61·9	+ 2·07
Amylic iodide.....	22·0	+ 3·67	64·6	+ 3·13
Amylic alcohol .....	16·0	— 4·52	76·0	— 4·12
Valeric acid..... <sup>1</sup>	11·0	+11·27	59·5	+10·84

in the states of liquid and vapour respectively are not greater than the errors of experiment, and all that can be asserted is that, under both conditions, the rotatory power has the same sign. For the other compounds, the rotatory power is of the same order of magnitude under both conditions, but is somewhat lower in the case of the vapours, a result which agrees with the observations of Gernez on other compounds. Valeraldehyde is the only compound which shows a marked difference of rotatory power between the two states, but its rotatory power varies with the time, and it seems to undergo condensation at its boiling point. Amylic alcohol vapour has a higher specific rotatory power than the liquid, which is contrary to the usual rule.

	$[\alpha]_D$	
	Liquid.	Vapour.
Valeraldehyde .....	+14·6	+ 7·1 to 6·4
Methylic valerate ...	+16·4	+14·3 „ 14·5
Amylic bromide ....	+ 2·8	+ 1·9
Amylic iodide.....	+ 5·6	+ 3·9 „ 4·1
Diamylamine.....	+ 6·3	+ 5·3 „ 5·9
Amylic alcohol .....	— 5·1	— 5·8 „ 6·5
Valeric acid.....	+13·5	+10·7 „ 10·9

C. H. B.

**Molecular Rotation and Molecular Deviation.** By PHILIPPE A. GUYE (*Compt. rend.*, 1895, 120, 876—877).—In reply to a recent criticism by Aignan, the author points out that he does not propose to substitute the molecular deviation for the molecular rotation. Neither of the two expressions gives a value which is independent of the conditions under which the polarimetric measurements are carried out, and to each therefore some correction has to be applied. The subject is being further investigated by the author. H. C.

**Guye's Formula.** By ALBERT COLSON (*Compt. rend.*, 1895, 120, 1416—1417).—The author again calls attention to some of the objections which he has raised to Guye's formula for the product of asymmetry (*Abstr.*, 1893, i, 457, ii, 105, 255; 1894, ii, 435). The enormous

variations which take place in the rotatory powers of certain liquids with changes in temperature show that Guyé's determinations are not sufficiently definite. Some of the numbers also change their sign if in place of yellow light other rays are employed; for the sense in which the variation in the rotatory power occurs in passing from one ray to another is not the same for all substances. For example, the following rotatory powers were determined at 15° in a layer 0.20 metre long.

	Line D.	Green line. (thallium).	Red line. (strontium).	
Methylic amylic oxide	20	10	—	decrease
Isoamylic oxide . . . . .	41	65	45	increase
Isobutylic amylic oxide	14	24	—	increase
Amylic acetate . . . . .	63	—	54	decrease

H. C.

**Magnetic Rotation of the Plane of Polarisation of Light in Liquids. Part I. Carbon Bisulphide and Water.** By JAMES W. RODGER and W. WATSON (*Proc. Roy. Soc.*, 1895, **58**, 234—237).—The aim of the investigation is the determination in absolute measure of the magnetic rotation of liquids at different temperatures, the effect of the chemical nature of the liquid on this property, and the correlation with other physical properties.

The results obtained for the rotation of carbon bisulphide may be summed up in the following equation, where  $\gamma t$  is the value of Verdet's constant at the temperature  $t$ ,

$$\gamma t = 0.04347 - 0.04737t.$$

The expression connecting rotation and temperature is therefore linear. In the case of water, the results are best represented by

$$\gamma t = 0.01311 - 0.04t - 0.04t^2.$$

Here the rate of change of the rotation with temperature increases as the temperature rises.

In the case of water, the quotient  $\gamma/\rho$ , where  $\rho$  is the density, is practically constant up to 20°, it then very slowly increases, the rate of increase between 20° and 100° being practically constant. For carbon bisulphide, the quotient  $\gamma/\rho$  decreases at a constant rate as the temperature rises, the rate of decrease being very much greater than the rate of increase in the case of water.

The measure of the molecular rotation which is usually employed in chemical investigations is

$$(M\gamma/\rho) \text{ substance}/(M\gamma/\rho) \text{ water},$$

where  $M$  is the molecular weight. Although the authors postpone a detailed discussion of the validity of this expression, they show that for carbon bisulphide, at any rate, its value changes with the temperature, and hence the conclusions obtained by its use regarding questions of chemical constitution, especially of tautomerism, are affected on this account.

They also point out that the above expression involves the properties of water. The only justification for the use of water in relative

observations is the elimination of variations in the strength of the magnetic field in which the observations are made. If the temperature of observation is always the same, this can readily be done. If, on the other hand, the temperature varies, it is essential to know how the rotation of water alters with the temperature. Up till now, the authors have made observations on eight liquids, besides water and carbon bisulphide, and in all cases except that of water the relation between rotation and temperature is linear, and the quotient, rotation divided by density, diminishes as the temperature rises. It is highly probable, therefore, that as regards magnetic rotation, as in the case of so many other properties, the behaviour of water is exceptional, and hence it is particularly ill suited for the use to which it has been put.

H. C.

**Electromotive Force of the Clark, Gouy, and Daniell Standards.** By C. LIMB (*Compt. rend.*, 1895, **121**, 199—200).—The author has determined the E.M.F. of the following standard cells.

Latimer Clark .....	1.4535 volts.
Gouy .....	1.3928 „
Daniell (Fleming type) .....	1.0943 „

The measurements were made at 0°.

H. C.

**Electrolysis of Gases.** By JOSEPH J. THOMSON (*Proc. Roy. Soc.*, 1895, **58**, 244—257).—In the experiments described in this paper, the spectroscope has been used to detect the decomposition of gases by the electric discharge and the movement of the ions in opposite directions along the discharge tube. A very simple method of showing the separation of the ions produced by the discharge of electricity through a compound gas such as hydrogen chloride, when the discharges through the constituent gases of the compound are of distinct and different colours, consists in the use of a capillary tube of very fine bore, the finer the better, with platinum wires for electrodes inserted in two small bulbs blown on the ends of the tube.

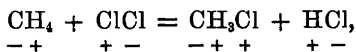
With hydrogen chloride at very low pressure, when first the discharge passes through the tube, the colour is uniform throughout and of a greenish-grey; after the discharge has been passing for a little time, the end of the tube next the cathode gets distinctly red, whilst that next the anode gets green, the discharge through hydrogen in a capillary tube being red, through chlorine green. When a tube is filled with hydrogen and a very small quantity of chlorine then let in through a side tube, after the discharge has been running through the tube for a short time, the chlorine spectrum is found to be bright at the positive electrode, although no trace of it can be detected at the negative. If the induction coil is reversed, so that what was before the positive electrode becomes the negative, the first effect observed is that the chlorine spectrum flashes out with greater brilliancy at the old positive electrode, and is much brighter than at any previous period. This, however, only lasts a second or two; the chlorine spectrum rapidly fades away, and for a time is not visible at either electrode, but it soon appears at the new positive electrode, having

been thus transferred from one end of the tube to the other. On again reversing the coil, the same phenomenon is repeated, and there is apparently no limit to the number of times this effect may be obtained, the chlorine being driven from one end of the tube to the other by reversing the coil. The same effect is obtained when a little bromine vapour is introduced into the tube instead of chlorine.

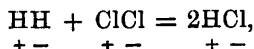
If a little vapour of sodium is introduced into the middle of a capillary tube filled with air at a low pressure, when the discharge is run through the tube the movement of the sodium vapour to the negative electrode is very apparent. When a small quantity of hydrogen is used in place of sodium vapour, the hydrogen also makes its way to the negative electrode.

When the discharge is passed through the vapour of sulphur monochloride, the chlorine lines are brighter at the negative than at the positive electrode, whilst the sulphur lines are brighter at the positive than at the negative. Thus the chlorine in this substance behaves in the opposite way to the chlorine in hydrogen chloride; in the latter compound, the chlorine ion has a charge of negative electricity, whilst in sulphur monochloride it has a charge of positive electricity. With the vapour of chloroform, it was found that both the hydrogen and the chlorine lines were bright on the negative side, whilst they were absent from the positive side, and that any increase in the brightness of the hydrogen lines was accompanied by an increase in the brightness of those due to chlorine. The spectrum on the positive side was that called the carbonic oxide spectrum. The appearance of the hydrogen and chlorine spectra at the same side was also observed in methylenic chloride and in ethylenic chloride. Even when all the hydrogen in methane was replaced by chlorine, as in carbon tetrachloride, the chlorine spectra still clung to the negative side. This is true also of silicon tetrachloride. From these experiments it would appear that the chlorine atoms in the chlorine derivatives of methane are charged with electricity of the same sign as the hydrogen atoms they displace.

When we can determine the signs of the electrical charges carried by the atoms in a molecule of a compound, we can ascertain whether any given chemical reaction does or does not imply interchange between the electric charges on the atoms taking part in the reaction. If we represent the sign of the charge of electricity carried by an atom by + or - placed below the symbol representing that atom, the following reaction,



can be produced by a rearrangement of the atoms without any alterations of their electrical charges. If, however, we take the reaction



we see that in addition to a rearrangement of the atoms there must in this case be an interchange of electric charges between the

atoms. We may thus distinguish between two classes of chemical reactions, (1) those which do not necessarily require any interchange of the electrical charges carried by the atom, and (2) those which do.

When the discharge first passes through the vapour of ethylic alcohol, the spectrum on the positive side is the candle spectrum, that on the negative side the carbonic oxide spectrum. If the discharge is kept running for some time, the candle spectrum on the positive side is replaced by the carbonic oxide spectrum, which now occurs on both sides, accompanied on the negative side by the hydrogen spectrum. This appearance was observed in many other cases.

With hydrogen alone, a striking change is observed in the relative brilliancy of the red and green lines at the two electrodes. On the positive side the red line tends to be brighter than the green, whilst on the negative side the green line tends to be brighter than the red. On the negative side, we have an excess of positively charged hydrogen atoms, whilst on the positive side there is an excess of negatively charged hydrogen atoms, and the difference in the spectra may be partly attributed to the difference in properties between a positively and a negatively charged hydrogen atom. No difference could be detected between the spectra given by chlorine at the two electrodes.

H. C.

**Velocities of the Ions.** By W. C. DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1895, 58, 182—187).—The author has directly measured the velocities of the ions during electrolysis by using solid solutions in agar-agar jelly, tracing the motion of the ion by the formation of a precipitate. The following table gives the velocities of all ions which have been experimentally determined.

	Specific ionic velocity in cm. per second.	
	Calc. from Kohl- rausch's theory.	Obs.
Hydrogen (in chlorides).....	0.0028	0.0026
„ (in acetates) .....	0.000048	0.000065
Copper .....	—	0.00031
Dichromate group ( $\text{Cr}_2\text{O}_7$ ).....	0.00047	0.00047
Barium .....	0.00037	0.00039
Calcium.....	0.00029	0.00035
Silver .....	0.00046	0.00049
Sulphate group ( $\text{SO}_4$ ).....	0.00049	0.00045
Cobalt in alcoholic $\text{CoCl}_2$ .....	—	0.000022
„ „ $\text{Co}(\text{NO}_3)_2$ ..	—	0.000044
Chlorine „ $\text{CoCl}_2$ .....	—	0.000026
Nitrate group „ $\text{Co}(\text{NO}_3)_2$ ...	—	0.000035

The sum of the ionic velocities of cobalt nitrate in alcohol, as calculated from the conductivity, comes out 0.000079, and that for cobalt chloride 0.000060. These numbers are to be compared with the sum of the observed velocities given above, namely, 0.000079 and 0.000048 respectively.

H. C.

**Dissociation of Cyanides.** By J. L. R. MORGAN (*Zeit. physikal. Chem.*, 1895, **17**, 513—535).—By the determination of the E.M.F. of the following chains (1)  $\text{Ag} \mid \text{AgNO}_3(\text{N}/10) - \text{KNO}_3(\text{N}/7) - \text{KCl}(\text{N}/1) \mid \text{HgCl} \mid \text{Hg}$ ; (2)  $\text{Ag} \mid \text{KAg}(\text{CN})_2(\text{N}/20) - \text{KNO}_3(\text{N}/1) - \&c.$ , and (3)  $\text{Ag} \mid (\text{KAg}(\text{CN})_2(\text{N}/20) + \text{MCN}) - \text{KNO}_3(\text{N}/1), \&c.$ , can be calculated the E.M.F. between (1) the  $\text{KAg}(\text{CN})_2(\text{N}/20)$  and the  $\text{AgNO}_3(\text{N}/10)$ , and (2) the  $[\text{KAg}(\text{CN})_2 + \text{MCN}]$  and the  $\text{AgNO}_3$ . Hence is obtained the ratio of the concentration of the silver ions in the two cyanide solutions, and from this ratio the concentration of the cyanide ions in the added cyanide, MCN. The dissociation of the double cyanide is shown to take place according to the scheme  $\text{KAg}(\text{CN})_2 \leq \overset{+}{\text{K}} + \text{Ag}(\bar{\text{CN}})_2$ ,  $\overset{+}{\text{K}} + \text{Ag}(\bar{\text{CN}})_2 \leq \overset{+}{\text{K}} + \text{AgCN} + \bar{\text{CN}}$  (to a smaller extent), and  $\text{AgCN} \leq \overset{+}{\text{Ag}} + \bar{\text{CN}}$  (to a very small extent), the concentration of the cyanide ions being about  $2.76 \times 10^{-3}$  N, and of the silver ions about  $3.65 \times 10^{-11}$  N in a N/20 solution. In other similar salts, as in  $\text{K}_2\text{Ni}(\text{CN})_4$ , the dissociation is similar, whilst potassium ferrocyanide also contains CN-ions, but to a much smaller extent than the foregoing, and in ammonium thiocyanate solution there is present only a very small percentage of CN-ions. The dissociation constant of hydrogen cyanide is found to be  $2.6 \times 10^{-8}$ , a number agreeing well with Van Laar's calculated value  $3.1 \times 10^{-8}$ . The method is also available for the determination of solubilities, and that of silver cyanide is so found to be  $3.17 \times 10^{-7}$  at  $17.5^\circ$ .  
L. M. J.

**Flames.** By NICOLAE TECLU (*J. pr. Chem.*, 1895, [2], **52**, 145—160; compare *Abstr.*, 1891, 1309; *Trans.*, 1892, 204, 322; 1894, 603).—The author describes some variations of his original apparatus for dividing flames (*Abstr.*, 1891, 1309) and the effects obtainable therewith. The principle involved in the construction of these apparatus has already been employed by Smithells and others.

In considering the combustion of illuminating gas, it is essential to take into account two flames—that of carbonic oxide and that of hydrogen. Apart from its yellow colour, due to glowing carbon, an illuminating gas flame is blue; such a colour appertains solely to the carbonic oxide, which is abundantly present as a product of combustion, and to the hydrogen in the flame. When coal-gas is allowed to stream into the air, there exist between the latter and the burner two zones, one of unburnt gas, the other a mixture of the gas and air. When kindled, the mixture of gases becomes a mass of glowing carbon and burning carbonic oxide and hydrogen; the products of this combustion pervade the flame, and, together with atmospheric nitrogen, detract from its luminosity. These reactions are dependent on the extent of the flame surface and, therefore, on the size of the burner and on the rate of issue of the gas.

When a mixture of air and gas is allowed to issue from a burner, the reactions are dependent on the rate of issue of the gas; for a mixture of hydrogen with oxygen will burn much more rapidly than a mixture of carbonic oxide with an equivalent volume of oxygen.

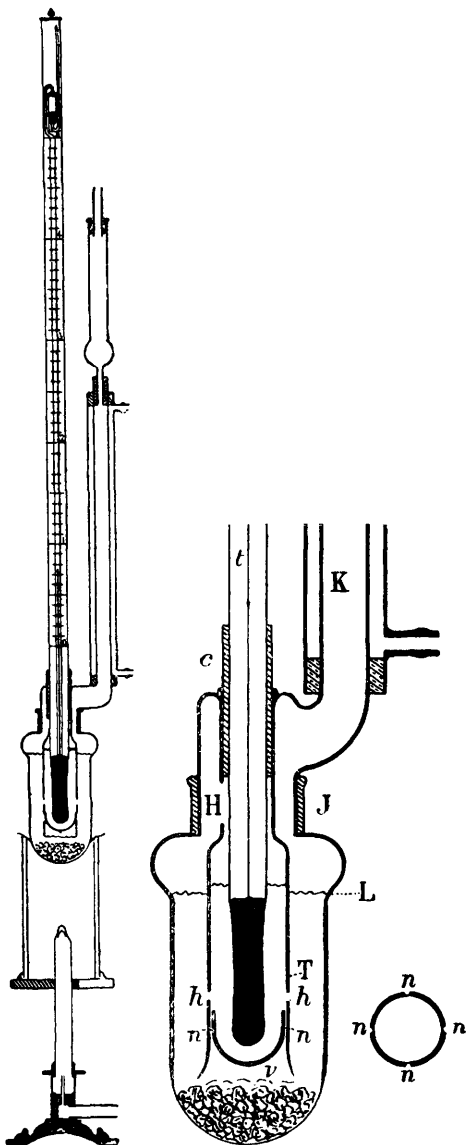


In consequence of this, the lower flame will consist mainly of burning hydrogen, the upper of burning carbonic oxide. Rapidity of diffusion may determine the partial reversal of this state of affairs in a burner with a long mixing tube. The proportion of oxygen, of products of combustion, and of inert gases present, is a modifying agency.

Some remarks on the colour of flames concludes the paper. A. G. B.

**New Boiling-point Apparatus for Molecular Weight Determinations.** By H. B. HITE

(*Amer. Chem. J.*, 1895, 17, 507—517).—The vessel, L, contains the solvent or solution, and in its lower part, to aid the boiling, are placed some glass beads, or, still better, some hollow balls, 3 mm. in diameter, of closely woven platinum gauze; it rests on a piece of wire gauze, supported on a piece of wide glass tubing, which serves as a chimney to the Bunsen burner used for heating; the flame should be a very small, smoky one. The vessel is closed by a ground glass stopper while the solvent is being weighed in it, but, during the determination, this is replaced by the ground stopper illustrated in the diagram. This on one side is prolonged into the condenser tube, K, through which the substance is introduced, and which at the upper end communicates with the air by means of a calcium chloride tube. In the centre, it is prolonged downwards into the tube T, which is closed at the lower end

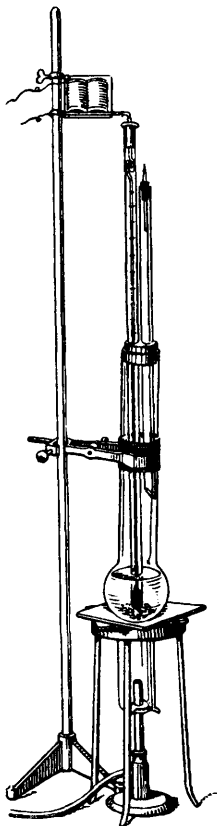


by the cup-shaped stopper sketched; this is ground to fit tightly for a length of 4—5 mm., and its upper (? lower) edge should be 20 mm. above the end of the tube T; three or four small vertical notches  $n, n$ , are filed on this stopper. The solution in the tube T communicates with that outside through the small holes  $h, h$ , and the vapour escaping from it passes through the hole H to the condenser. When the apparatus is working, vapour given off in bubbles at the bottom of the flask collects in the space  $v$ , and passes upwards through the notches  $n, n$ , in a series of small bubbles through the liquid in T, in which the bulb of the Beckmann thermometer is placed; this liquid is thus kept well stirred, and it is protected against superheating by the jacket of solution. It is claimed that the apparatus is simpler than Beckmann's, and gives better results; in experiments made with alcohol, ether, and benzene as solvents, the results of individual determinations never varied by more than 10, and seldom by more than 5, per cent.

C. F. B.

### New Boiling-point Apparatus for Molecular Weight Determinations.

By WILLIAM R. ORNDORFF and F. K. CAMERON (*Amer. Chem. J.*, 1895, **17**, 517—531).—The bulb-tube, which may be part of a V. Meyer vapour density apparatus, should be about 300 mm. long by 40 mm. in diameter, and is preferably of thin glass; it contains the solution, and its bottom is covered with pellets made by rolling together strips of scrap platinum; the use of 30—40 grams of these is suggested. The condenser is a plain tube of about 13 mm. diameter, with its lower end ground obliquely so as to return the condensed liquid down the sides of the bulb-tube; its upper end is closed by a piece of tubing with a capillary orifice or by a calcium chloride tube; when a low-boiling solvent is employed, this tube is lengthened and provided with a water-jacket. Slightly above the lower end of the condenser a strip of fine copper gauze, 4 cm wide, is wound three or four times round the tube of the outer bulb, and is gripped by the bare metal of the clamp; this arrangement acts as a condenser, so that very little vapour condenses in the upper part of the tube. The tube rests on wire gauze placed over a circular orifice, 30—40 mm. in diameter, in a piece of thick asbestos cardboard, and is strongly heated so as to cause a rapid boiling of the solution. A Beckmann thermometer is used, and is tapped by an electric hammer made from a small electric bell with the gong removed; it is better that the thermometer should have a capillary tube of wider bore than is usual, although the



larger bulb thus necessitated is a disadvantage. The apparatus is less troublesome, and requires less time, to work than Beckmann's, and is especially useful for high-boiling solvents; experiments were made with carbon bisulphide, chloroform, benzene, toluene, pyridine, ethylenic bromide, anisole, phenetole, and naphthalene as solvents, and the results of individual determinations never differed by more than about 10 per cent., and were usually much less than this.

C. F. B.

**Motions of and within Molecules; and on the Significance of the Ratio of the two Specific Heats in Gases.** By G. JOHNSTONE STONEY (*Proc. Roy. Soc.*, 1895, 58, 177—182).—We may distinguish the movements of molecules into three kinds of events.

1. A events; by which are to be understood motions of the centres of mass of the molecules relatively to one another.

2. Ba events; that is, events within a molecule which act on and are reacted on by a neighbouring molecule, if sufficiently near.

3. Bb events; more isolated events going on within molecules, events of the kind that manifest themselves conspicuously in phosphorescent substances, events which but slowly part with any excess of energy they may possess to the other events going on within the molecule, or to neighbouring molecules.

An event of the Bb class, which subsides so rapidly as to require the phosphoscope to detect it, will behave, in any protracted experiment for determining the ratio of the two specific heats, in the same way as events of the Ba class. But this ceases to be the case where the ratio of the two specific heats is determined by experiments on sound; and in all the experiments which have been made use of it ceases to be the case when Bb events are as slow in subsiding as some of them are in conspicuously phosphorescent substances.

Now the method by which the ratio of the two specific heats has been determined for argon and helium has been by experiments on sound; and as the value furnished by this method depends on Ba events, it is competent to supply information about them only. It gives no information as to the energy involved in events of the Bb class. Accordingly it remains quite possible that Bb events may be easily evoked by stimulation of argon and helium, and that while in existence they may engross a considerable share of the total energy in the gas. That this is the case would seem to be evidenced by the vivid spectra which these gases exhibit under the influence of electricity. There appears, therefore, to be no ground for the supposition which has been sometimes entertained, that there is incompatibility between the two facts that have been observed—the fact that in these two gases the ratio of the two specific heats is near its maximum value, and the fact that these gases, when stimulated by electricity, furnish brilliant spectra.

If the molecule consists of but one chemical atom, there may be both Ba and Bb events going on within that so-called atom. If the molecule consist of two or more chemical atoms, a part of the Ba events may be motions of the centres of mass of these atoms relatively to one another. But this is not always the case: the bonding between the atoms that form the molecule may be such that there is

but little of this relative motion. Accordingly, the ratio of the two specific heats being large does not necessarily imply that the molecule is monatomic. The inference involves the erroneous supposition that there are no events going on within the molecule, and few degrees of freedom in its motion.

H. C.

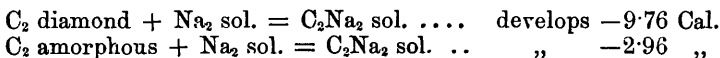
**Specific Heat of Superfused Salts.** By LOUIS BRUNER (*Compt. rend.*, 1895, **121**, 60—61). The author has measured the specific heat of liquid sodium thiosulphate with the following results.

Temp.	Sp. heat.	Temp.	Sp. heat.
94—17°	0·584	55—16°	0·599
83—16	0·586	47—17	0·602
83—16	0·588	36—17	0·395
65—16	0·590	2—13	0·563

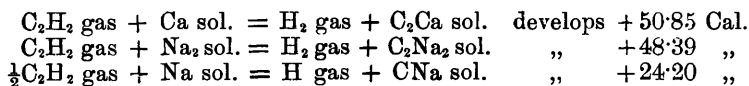
The maximum occurs at about the fusing point, 48°. H. C.

**Heat of Formation of Sodium Acetylides.** By ROBERT DE FORCRAND (*Compt. rend.*, 1895, **120**, 1215—1218).—Sodium acetylide is readily obtained by heating the metal to dull redness in a current of dry acetylene, but a considerable quantity of carbon separates at the same time, and remains mixed with the product. The volume of acetylene evolved by the action of water corresponds exactly with the weight of sodium as determined by titration. It follows that the acetylides contains no free sodium, nor any compounds such as  $\text{Na}_2\text{H}$  or  $\text{C}_2\text{NaH}$ , and the carbon is simply mixed with it. It alters rapidly and deliquesces when exposed to air, and also oxidises readily.

Dissolution in dilute sulphuric acid leads to the following results.



the values being somewhat lower than with calcium carbide.



Correcting the last value for the heat of volatilisation of solid acetylene on the assumption that it is one-third of that of solid benzene, it becomes +22·65 Cal.

It would seem that the thermal value of the hydrocarbon function is about +23 Cal, which is lower than the alcoholic function of the tertiary alcohols, and differs from the latter about as much (+5·24 Cal.) as they differ from the primary alcohols (+3·98). The difference between primary alcohols and phenols is greater (+7 Cal.).

C. H. B.

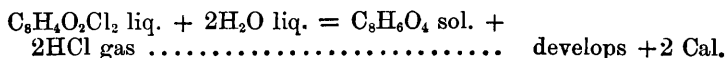
**Calorimetric Investigations. Heat Equivalents of the Amides and Anilides of Monobasic acids.** By FR. STOHMANN and RAYMUND SCHMIDT (*J. pr. Chem.*, 1895, [2], **52**, 59—71).—The amides and anilides of some monobasic acids, chiefly fatty, have been investigated. Isomeric substances have practically the same heat

equivalents, except that benzamide differs considerably from form-anilide, as one would expect from the previously known cases of such isomerism. An homologous difference of  $\text{CH}_2$  produces a difference of 156.6 in the heat equivalent, just as in the case of the acids themselves; as is commonly found, however, the difference between the propionic and acetic derivatives is distinctly greater than this number, and that between the acetic and formic derivatives very decidedly less. The heat equivalents of the amides and anilides are greater by 75.9 and 804.6 Cal. respectively than those of the corresponding acids. The heat equivalent of the change, acid + ammonia (gaseous) = amide + water is +15.2 Cal., and that of the change, acid + aniline (liquid) = anilide + water is +6.0 Cal. The actual experimental results are given below.

	Amide.		Anilide.	
	Heat equivalent.	Heat of formation.	Heat equivalent.	Heat of formation.
Formic .....	134.9	62.6	861.4	38.1
	(liquid)			
Acetic .....	282.7	77.8	1010.8	51.7
Propionic .....	439.8	83.7	1168.0	57.5
Butyric .....	596.1	90.4	1324.3	64.2
Isobutyric .....	596.0	90.5	—	—
Isovaleric .....	751.6	97.9	—	—
Lauric .....	1849.7	140.8	2578.4	114.1
Myristic .....	2160.6	155.9	2891.4	127.1
Palmitic .....	2472.9	169.6	3204.9	139.6
Benzoic .....	847.8	51.7	1576.3	25.2
[Ammonium formate....]	129.5	137.0]	—	—

C. F. B.

**Phthalic Chloride and Phthalide.** By PAUL RIVALS (*Compt. rend.*, 1895, 120, 1218—1219). The heat of combustion of phthalic chloride is 804.69 Cal. at constant volume, and 804.41 Cal. at constant pressure, and the heat of formation of the liquid chloride from its elements is therefore +97.8 Cal.



This value is very different from that obtained with benzoic chloride or toluic chloride. Moreover, the heats of formation of solid benzene, benzoic acid, and phthalic acid show a regular increase, but no such sequence obtains with liquid benzene, benzoic chloride, and phthalic chloride. It would seem, therefore, from thermochemical as well as purely chemical considerations, that phthalic chloride is not the symmetrical chloride of a dibasic acid, but a dissymmetrical isomeride. It is possible that phthalic chloride, like succinic chloride, may be a mixture of the two isomerides.

The heat of combustion of phthalide is 883.87 Cal. at constant volume, and 884.15 Cal. at constant pressure, and its heat of formation in the solid state is +77.25 Cal. No regular order is observed between the heats of formation of benzene, benzaldehyde, and phthalide.

The heat developed by the substitution of chlorine for hydrogen in phthalide, with production of phthalic chloride  $32.3 \times 2$  Cal. is comparable with that developed by the substitution of chlorine for hydrogen in the paraffin series. C. H. B.

**Campholenic Lactones (Olides).** By MARCELLIN BERTHELOT and PAUL RIVALS (*Compt. rend.*, 1895, 120, 1390—1391).—The inactive campholenic lactone, prepared by Béhal, and melting at 30°, has a heat of combustion at constant pressure of +1351.2 Cal., and its heat of formation from its elements is +143.8 Cal.; for the dextrogyrate lactone the corresponding values are +1354.1 Cal. and +140.9 Cal. respectively, the difference between the two compounds being not greater than the experimental error.

It is noteworthy that the heat of formation of these lactones is distinctly higher than that of the campholenic acids, with which they are isomeric; the difference between the inactive lactone and the liquid campholenic acid is +12.1 Cal. C. H. B.

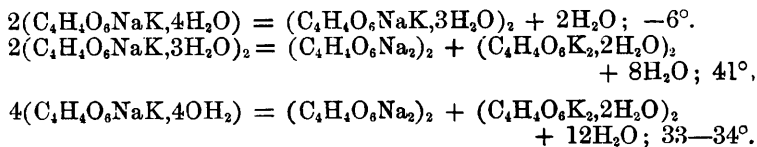
**Calculation of the Heat of Dissolution.** By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1895, 17, 545—549).—The author considers that owing to the change of the dissociation constant by the dissolution of a quantity  $ds$  of the dissolved substances ( $s$  being the gram molecules of the substance present in 1 gram molecule of the solvent), a correction must be applied to the expression deduced by Rudolphi (this vol., ii, 435); whilst the same applies to the expression employed by van't Hoff (*Zeit. physikal. Chem.*, 17, 147). By making this correction, the value  $L = W + a/2 - a Q$  is obtained instead of  $L = W + a/Q$ , and the values for the heat of solution in the cases examined by Rudolphi are recalculated. L. M. J.

**Calculation of the Heat of Dissolution.** By HANS JAHN (*Zeit. physikal. Chem.*, 1895, 17, 550—551).—The values obtained by Rudolphi are recalculated by the author employing a somewhat different expression, the heat developed being given by the formula  $L = -T^2/(C_1 + C_2) (dC/dT + 2C_2/dT)$ . L. M. J.

**Heat of Dissolution and Neutralisation of Campholenic acids.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 1392).—The heat of neutralisation of the liquid campholenic acid is +13.2 Cal., and it behaves as a normal monobasic acid; its heat of dissolution in water is very small. The heat of neutralisation of the solid acid is also +13.2 Cal., and it likewise behaves as a normal monobasic acid; its heat of dissolution is -3.2 Cal.

The heat of neutralisation of campholic acid is between +10 and +15 Cal., and is probably normal; the heat of dissolution of the solid acid in sodium hydroxide solution is +10.0 Cal. C. H. B.

**Wyrouboff's Racemate.** By JACOBUS H. VAN'T HOFF and HEINRICH GOLDSCHMIDT (*Zeit. physikal. Chem.*, 1895, **17**, 505—512).—The authors first verified Wyrouboff's statements concerning the formation of the double racemate of potassium and sodium from a mixture of + and - tartrates at a temperature of about  $-6^{\circ}$ . The transition temperature of a mixture of single racemates was next obtained by both thermometric and dilatometric methods; and also by the thermometric and tensimetric methods, the transition temperature from the mixture of the + and - racemates to the single racemates. The results obtained were as follows.



The results are seen to be closely analogous to those found with Scacchi's salt. (This vol., ii, 380). L. M. J.

**Racemism, and Changes of Temperature on Mixing Liquids.** By ALBERT LADENBURG (*Ber.*, 1895, **28**, 1991—1995).—In his previous paper (this vol., i, 253), the author did not assume, as is stated by E. Fischer (*Ber.*, **28**, 1153), that it is sufficient proof of the racemic nature of a compound when development or absorption of heat takes place on mixing the two optically active isomerides to form an inactive substance, but that if a change of temperature occurs without a simultaneous alteration in the specific gravity, the conclusion may be drawn that a racemic derivative is formed, and not merely an inactive mixture of the two components. To this statement, the author still adheres, and, in confirmation of the supposition, he finds from a number of experiments, details of which are given, that when two substances of approximately the same specific gravity, and having no chemical action on each other, are mixed, scarcely any change of temperature occurs, whilst if the specific gravity of the two liquids differs, considerable changes of temperature are observed, these becoming greater as the differences in the specific gravity of the two substances increases; the specific gravity of the mixture then always differs considerably from that calculated from the specific gravity of the components.

The author has confirmed the fall of temperature which takes place when equal quantities of dextro- and lævo-coniine are mixed, but finds that no change of temperature occurs when dextro- and lævo-limonene are mixed, and therefore the resulting dipentene is not a racemic derivative, but simply an inactive mixture of the two components. H. G. C.

**Determination of the Specific Gravity of Solids.** By THE EARL OF BERKELEY (*Min. Mag.*, 1895, **11**, 64—68).—An ordinary pyknometer with a thermometer stopper and a side capillary tube is used. The principle of the method consists in waiting until the evaporation

at the stopper brings down the level of the enclosed liquid (carbon tetrachloride) to the mark on the side tube, the temperature being noted at the time of weighing; the capacity of the pyknometer and the density of carbon tetrachloride having been previously determined for different temperatures and plotted on curves. The results are accurate to one part in 2000.

L. J. S.

**The Vapour Pressure of the Combined Water in Copper Sulphate and Barium Chloride.** By WILHELM MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, 1895, 17, 446—458).—By the comparison of the loss of weight by evaporation from hydrated salts and pure water under similar conditions, the vapour pressure of the combined water in the former is calculable. In certain cases, however, as in copper sulphate and barium chloride, the results thus obtained do not agree among themselves, nor with the results according to the statical method. The author has therefore repeated and re-examined the evaporation experiments, and as the ratio of the evaporation remains constant for different pressures he concludes that the action is not merely a surface action as Tammann supposed. Different samples of copper sulphate, although apparently chemically identical, were found to give different initial values and to take different times before attaining their maximum value. By allowing the salts examined to become fully hydrated in damp air and again taking the measurements, concordant results are, however, obtainable, and by this means the author obtained satisfactory values for the salt examined. The ratio of the vapour pressure of copper sulphate to that of water was in this way found to be 0.25 at 12°, and that of barium chloride 0.15 at 13°, numbers agreeing satisfactorily with those given by the statical method.

L. M. J.

**Volume of Salts in their Aqueous Solutions.** By PAUL E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, 120, 1190—1192).—The changes of volume which accompany dissolution may sometimes with advantage be directly determined in a dilatometer, consisting of a flat-bottomed flask of 75 to 125 c.c. capacity with a somewhat large neck, fitted with a good cork carrying a graduated tube of small diameter. The finely powdered salt, in a constant state of hydration, is placed in a tube of convenient height closed at one end, and covered with recently boiled petroleum of sp. gr. about 0.82. Recently boiled water is placed in the flask, the tube containing the salt is introduced, and the flask is filled up with more of the same petroleum. When the temperature is constant, the position of the petroleum in the graduated tube is read off, the salt in the small tube is brought in contact with the water, and after dissolution is complete and the temperature is the same as before, the position of the petroleum is again read off. By operating in this way, any traces of air adhering to the salt are somewhat rapidly dissolved by the boiled water and petroleum.

By comparing the results obtained by the dilatometer with those obtained by the ordinary bottle method, the true sp. gr. of the salt can be calculated. If  $V$  be the volume of the salt according to its provisional sp. gr.,  $w$  the true volume corresponding with the true sp. gr.,



$p$  the true percentage change of volume compared with the true volume of the solid, the volume of the water being regarded as constant,  $M$  the percentage change of volume by the bottle method, on the basis of the provisional sp. gr., and  $N$  the percentage change of volume by the dilatometer method, also on the basis of the provisional sp. gr. Then, by the bottle method,  $w + \frac{wp}{100} - V$  is the change of volume referred to the provisional sp. gr., and hence

$$V : w + \frac{wp}{100} - V :: 100 : M \text{ and } w = \frac{100V + MV}{100 + p}.$$

With the dilatometer  $V : \frac{wp}{100} :: 100 : N$ ,

and hence 
$$p = \frac{100N}{100 + M - N}.$$

The two methods control one another, and the author finds for the sp. gr. of sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ , 1.751, and for sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ , 1.448. C. H. B.

**Volumes of Salts in their Aqueous Solutions.** By PAUL E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, 121, 100—102).—The dilatation which occurs when ammonium chloride and other ammonium salts are dissolved in water at the ordinary temperature, is usually regarded as an anomaly due to the peculiar constitution of these compounds. It is, however, quite possible that the ammonium salts merely occupy one extreme end of a series, at the other extremity of which may be placed those salts which cause the greatest contraction. When a salt is dissolved in water, the accompanying volume change is made up principally (1) of the dilatation caused by the fusion of the salt without decomposition at the temperature of the experiment, and (2) of the contraction due to the combination of the salt with the solvent, this combination becoming more marked the more dilute the solutions and the lower the temperature. In keeping with these views, the author finds that ammonium chloride always causes a dilatation on solution in water at 15°, but that at 0° there is a slight contraction for very dilute solutions. And sodium thiosulphate which causes an enormous contraction at 15° in dilute solution, produces dilatation in very concentrated solution. H. C.

**Osmotic Phenomena between Ether and Methylic Alcohol with Different Diaphragms.** By FRANÇOIS M. RAOULT (*Compt. rend.*, 1895, 121, 187—189).—The osmometer used by the author consists of a cylindrical box of bronze, divided by means of a permeable partition into two compartments, each of 100 c.c. capacity, and each communicating with a vertical manometer tube. When the two compartments are filled with different liquids, osmose takes place as a rule, and passage of the one liquid into the other through the permeable partition; then the liquid sinks in one of the manometer tubes, and rises in the other. In the experiments recorded

the liquids used were ether and methylic alcohol. If the permeable diaphragm is one of pig's bladder, osmose, that is passage of liquid, takes place,

1. From methylic alcohol into pure ether ;
2. From methylic alcohol into a mixture of one-fifth ether and four-fifths methylic alcohol ;
3. From a mixture of one-fifth methylic alcohol and four-fifths ether into pure ether.

The diaphragm behaves as if impermeable to ether and permeable to methylic alcohol, and the velocity of the passage of the alcohol through the diaphragm is inversely proportional to the quantity of ether previously mixed with the alcohol. If the permeable partition is one of vulcanised india-rubber, 1 mm. in thickness, osmose takes place in the reverse sense, and a passage of liquid,

1. From pure ether into methylic alcohol ;
2. From a mixture of one-fifth ether and four-fifths methylic alcohol into pure methylic alcohol ;
3. From pure ether into a mixture of one-fifth methylic alcohol and four-fifths ether.

The vulcanised india-rubber diaphragm behaves, therefore, as though impermeable to methylic alcohol and permeable to ether. A measurement of the pressure which this osmose is capable of producing presents great difficulty, and the author has only been able to establish the fact that it is very considerable. A mixture of equal volumes of ether and methylic alcohol was separated from pure ether by means of an india-rubber diaphragm. Osmose took place, and the pressure on the side of the mixture rose to 50 atmos. without any apparent decrease in the velocity of the osmose. Fracture of the manometer prevented further measurement.

The experiments show that osmose between two liquids may not only vary in energy, but even change in sense with change in the character of the diaphragm, and that the osmotic movement of substances through a diaphragm may be perfectly independent of their molecular weights, or of their character as dissolved substances or solvents.

H. C.

**Determination of Isosmotic Concentrations.** By H. KÖPPE (*Zeit. physikal. Chem.*, 1895, **17**, 552—553).—The differences between the results of Hedin (this vol., ii, 381) and those of the author are regarded as due to the fact that the solutions actually examined are not the solutions added, but are these diluted by the plasma of the blood.

L. M. J.

**Water of Crystallisation.** By THEODOR SALZER (*Ber.*, 1895, **28**, 2033—2038; compare *Abstr.*, 1894, ii, 416).—The author adduces evidence in support of the regularities to which he has already drawn attention (*Annalen*, 1886, **233**, 1), underlying the phenomena of water of crystallisation.

M. O. F.

**Solubility of Superfused Salts.** By LOUIS BRUNER (*Compt. rend.*, 1895, **121**, 59—60).—According to Walker (*Abstr.*, 1890, 686), the

curves for the solubility of the same substance in the liquid and solid states cut one another at the melting point. The solubility of the solid substance above the fusing point will be greater than that of the liquid, below the fusing point it will be less. The latter condition is the only one that can be realised in practice. The author has compared the solubilities of solid and of superfused sodium thio-sulphate in alcohol; he finds, in keeping with the above, that the superfused salt has the greater solubility. H. C.

**Solubility of Benzene Derivatives in Water.** By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], 52, 72—75).—A table of the solubility of a number of aromatic substances is given, and the following general inferences are drawn. "The solubility of these substances is conditioned by the presence of an amido, hydroxyl, or carboxyl group. The 'dissolving force' (*lösende Kraft*) of these is weakened by the presence of substituting groups, such as methyl, bromine, iodine, and the nitro-group. The methyl group lowers the solubility most when it is in the para-, least when in the ortho-, position, and the same holds for the nitro-group, bromine, and iodine, in the substituted benzoic acids. In the amido- and hydroxy-derivatives, on the other hand, the influence of the nitro-group is greatest in the ortho-, least in the meta-, position. In the case of isomeric derivatives, the meta-substituted compound has the greatest, the para-substituted the least, solubility." In the case of aniline, the solubility is increasingly diminished by the successive replacement of the two amido-hydrogen atoms by alkyl groups. Carnelley and Thomson's rule, that for isomeric organic compounds the order of solubility is the same as the order of fusibility, does not hold. C. F. B.

**Solubility of Carbon Compounds in Carbon Bisulphide at Low Temperatures.** By HENRYK ARCTOWSKI (*Compt. rend.*, 1895, 121, 123—125).—The author has determined, by Étard's method, the solubility of various substances in carbon bisulphide at low temperatures. The melting point of the bisulphide is  $-115^{\circ}$ ; the results are stated in grams of the substance contained in 100 grams of the saturated solution at the specified temperature. Mercuric iodide, 0.017 at  $-116^{\circ}$ ; iodine, 0.378 at  $-94^{\circ}$ ; sulphur, 2.99 at  $-116^{\circ}$ ; stannic iodide, 9.41 at  $-114.5^{\circ}$ ; bromine, 36.9 at  $-116^{\circ}$ ; phthalic anhydride, 0.016 at  $-77.5^{\circ}$ , 0.013 at  $-93^{\circ}$ , 0.013 at  $-112.5^{\circ}$ ; triphenylmethane, 1.91 at  $-83^{\circ}$ , 1.56 at  $-91^{\circ}$ ; 1.24 at  $102^{\circ}$ , 0.98 at  $-113.5^{\circ}$ ; diphenylamine, 0.87 at  $-88.5^{\circ}$ , 0.37 at  $-117^{\circ}$ ; naphthalene, 1.38 at  $-82^{\circ}$ , 1.05 at  $-89.5^{\circ}$ , 0.62 at  $-108.5^{\circ}$ .

These results show that not only does the solubility not become zero at the freezing point of the solvent, as Étard has concluded, but the curves of solubility do not tend towards the same point, and do not tend to cut the axis of temperatures, but are asymptotic with it. C. H. B.

**Molecular Symmetry and Asymmetry.** By ALBERT LADENBURG (*Ber.*, 1895, 28, 1995—1997).—It is usually supposed that when the molecule of a substance contains no plane of symmetry, the substance

is capable of existing in two enantimorphic forms, each being the reflected image of the other. The author points out that there are certain exceptions to this rule, namely, such substances as contain a pseudo-plane of symmetry, that is a plane which divides the molecule into two parts, one of which has the same relation to the other as an object to its image in a plane mirror. In such cases, the image of the whole molecule is also identical with the object, and therefore no enantimorphic forms are possible.

H. G. C.

**Calculation of Affinity Constants.** By MAX RUDOLPHI (*Zeit. physikal. Chem.*, 1895, **17**, 385—426).—In the case of many acids and salts, the dilution law for the dissociation is not obeyed, that is, the expression  $(\lambda_v/\lambda_\infty)^2/v(1 - \lambda_v/\lambda_\infty)$  does not lead to a constant ( $k$ ). Thus, for silver nitrate,  $k_{18} = 0.26$ ,  $k_{34} = 0.13$ ,  $k_{256} = 0.065$ , numbers which evidently indicate the constancy of  $k\sqrt{v}$ , that is, of  $(\lambda_v/\lambda_\infty)^2/\sqrt{v(1 - \lambda_v/\lambda_\infty)}$ . The value of this expression is therefore determined for a large number (128) of salts and acids, and is found to be dependent on the nature of the electrolyte and solvent, but independent of volume and temperature. Analogous salts of similar elements have approximately the same constant; this result also obtains for analogous acids. Chlorides, bromides, iodides, fluorides, and nitrates have a similar constant, as have carbonates and sulphates, whilst in all cases the constant of the acid is greater than that of the corresponding salts.

L. M. J.

**The Influence of Centrifugal Force on Chemical Systems.** By GEORG BREDIG (*Zeit. physikal. Chem.*, 1895, **17**, 459—472).—If a gas be enclosed in a rotated tube then the variation of pressure is given by the equation  $dP/P = 4\pi^2 n^2 r^2 M dr/RT$ , where  $r$  is the radius of rotation,  $n$  the number of turns per second, and  $M$  the molecular weight of the gas. From this, can be readily derived that if a mixture of two gases be rotated, their *relative* molecular concentrations ( $c_1$  and  $c_2$ ) at radii  $r_1$  and  $r_2$  are given by the equation  $\log(c_1/c_2) = (r_1^2 - r_2^2)(M' - M'')2\pi^2 n^2/RT$ , so that the relative concentration of the gas of higher molecular weight increases with the radius of rotation. A tube consisting of two portions connected by means of a stopcock was therefore filled with a mixture of hydrogen and hydrogen iodide, and was rapidly rotated for from  $1\frac{1}{2}$  to 3 hours when it was stopped, and the stopcock immediately closed. Owing to the stoppage, the sum of the partial pressures will now be equal in the two halves of the tubes, but the relative concentrations will not have been greatly altered, and the ratio of the partial pressure of the hydrogen in the two halves can be theoretically obtained. It was experimentally determined by the absorption of the hydrogen iodide in each part by a potash solution, the values so obtained, 0.970, 0.975, and 0.972, agreeing very satisfactorily with the calculated numbers 0.986, 0.979, and 0.982. The effect of centrifugal force on a system in equilibrium is also considered, and the result obtained that, although the density of the system increases with the radius, the equilibrium constant is not altered. The author points out that water in a rotated tube would distil to the far end owing to the diminution of

the density of the vapour at the nearer end, and discusses shortly the compensation effect due to temperature difference consequent on the evaporation and condensation.

L. M. J.

**Precipitates in Gelatinous Solutions.** By NATHANAEL PRINGSHEIM (*Zeit. physikal. Chem.*, 1895, **17**, 473—504).—A graduated tube was filled with gelatin and placed horizontally in communication with two vessels containing liquids capable of forming a precipitate. After a time, owing to diffusion, a precipitate is formed within the gelatin, and this precipitate, it is observed, may increase in thickness towards either side, but not towards both, the direction in which the increase takes place depending on the concentrations of the solutions. In some cases, the increase ceases shortly after the formation of the precipitate, and in experiments with potassium chloride—silver nitrate, barium chloride—silver nitrate, potassium ferrocyanide—copper sulphate, potassium dichromate—lead acetate, the limited increase occurred when the solutions were at, or nearly at, equivalent concentrations. If the concentrations were not nearly equivalent, unlimited increase took place on the side of the solution of lower concentration. The author also observed a slight movement of the precipitate shortly after its formation, and this motion is proved to be real, and not an apparent motion due to contraction or expansion of the gelatin. It was found to be independent of the concentration of the solutions and to depend only on their nature, being in the cases examined in the directions  $\text{AgNO}_3 \rightarrow \text{KCl}$ ;  $\text{CuSO}_4 \rightarrow \text{K}_4\text{FeC}_6\text{N}_6$ ;  $\text{K}_4\text{FeC}_6\text{N}_6 \rightarrow \text{ZnSO}_4$ , and  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \rightarrow \text{K}_4\text{FeC}_6\text{N}_6$ . A list of the diffusion velocities in the cases examined is also added, and the foregoing results, and the question of the use of these precipitates in osmotic experiments are shortly discussed.

L. M. J.

**Systematic Arrangement of the Elements.** By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1895, **9**, 190—193).—The author arranges the elements in ascending order of atomic weights in three main groups, of which the first contains two series of seven elements, the second two series of 17 elements, and the third 31 elements. Hydrogen stands by itself. Electropositive elements are at the one end of each of the four smaller series and electro-negative elements at the other. The arrangement serves to show relationships between the elements beyond those shown by the ordinary periodic scheme.

E. C. R.

**Methods of Physico-chemical Measurements.** By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1895, **17**, 427—445).—The author briefly reviews and discusses the aims and methods of physical chemistry.

L. M. J.

**A Gas Furnace.** By C. BIGOT (*Zeit. anal. Chem.*, 1895, **34**, 447—448; from *Mon. sci.*, **37**, 519).—This furnace, which is capable of giving any desired temperature up to one exceeding the melting point of porcelain, with either a reducing or oxidising atmosphere, is heated by a ring of bunsen burners, from which the gas, passing

into the interior of an outer chamber, there meets air heated by entering round the flue. The products of combustion then pass downwards through an inner chamber, where the object to be heated is situated, and escape by a descending flue to a chimney. A figure is given.

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M. J. S.

## Inorganic Chemistry.

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**Occlusion of Oxygen and Hydrogen by Platinum Black.** By LUDWIG MOND, WILLIAM RAMSAY, and JOHN SHIELDS (*Proc. Roy. Soc.*, 1895, **58**, 242—243; and *Zeit. anorg. Chem.*, **10**, 178—180).—The authors describe experiments on the occlusion of oxygen and hydrogen by platinum sponge and foil which confirm the results obtained by Graham.

Platinum black dried at  $100^{\circ}$  contains 0.5 per cent. of water, and this can only be removed in a vacuum at about  $400^{\circ}$ , at which temperature the black is converted, at least partially, into sponge. At any given temperature, the water retained by platinum black seems to be constant. The density of platinum black dried at  $100^{\circ}$  is 19.4, or, allowing for the water retained by it, 21.5. Platinum black contains altogether about 100 volumes of oxygen; this begins to come off in quantity at  $300^{\circ}$  in a vacuum, and the bulk of it can be extracted at  $400^{\circ}$ , but a red heat is necessary for its complete removal. Small quantities of carbonic anhydride are also extracted, chiefly between  $100^{\circ}$ — $200^{\circ}$ . About 310 volumes of hydrogen are absorbed per unit volume of platinum black, but of this 200 volumes are converted into water, and only 110 volumes are really occluded by the platinum. Part of it can be again removed at the ordinary temperature in a vacuum, and by far the larger portion at about  $250^{\circ}$ — $300^{\circ}$ , but a red heat is necessary for its complete removal. The amount of hydrogen absorbed by platinum is very largely influenced by slight traces of impurity.

Platinum black in a vacuum absorbs a certain quantity of hydrogen, and on increasing the pressure to about 200—300 mm. a further quantity is absorbed. After this, however, pressure is almost without effect, for by increasing the pressure from one atmosphere to  $4\frac{1}{2}$  atmospheres, only one additional volume of hydrogen was absorbed. On placing platinum black, charged with oxygen, in an atmosphere of oxygen, and increasing the pressure to the same extent,  $8\frac{1}{2}$  volumes were absorbed. Platinum black, charged with hydrogen, in an atmosphere of hydrogen at atmospheric pressure and platinum black, charged with oxygen, in an atmosphere of oxygen behave quite differently when heated. In the former case, hydrogen is expelled, whilst in the latter case oxygen is gradually absorbed until a temperature of  $360^{\circ}$  is reached, when, on further heating, oxygen begins to come off.

The authors point out that there is not sufficient evidence for the existence of such compounds as  $\text{Pt}_{30}\text{H}_3$  and  $\text{Pt}_{30}\text{H}_2$ . Moreover, the heats

of combination of hydrogen and platinum as determined by Berthelot and Favre are valueless; the heat which they measured is due to the formation of water by the oxygen always contained in platinum black.  
E. C. R.

### Properties of Ozone, and of Oxygen in presence of Sunlight.

By J. ADOLPHE BESSON (*Compt. rend.*, 1895, **121**, 125—128).—When tetrachlorethylene is exposed to light in presence of excess of oxygen, it is converted into trichloroacetic chloride and carbonyl chloride, the action being more rapid under slightly increased pressure. The same products are formed by the action of ozone (*Abstr.*, 1894, i, 481). No compound such as  $(\text{CCl}_2)_2\text{O}$  seems to be formed. This result explains the apparently complete oxidation of tetrachlorethylene by hydrogen peroxide under the influence of sunlight; the final products result from the action of the water on the direct oxidation products of the tetrachlorethylene.

Phosphorus trichloride is completely converted into phosphorus oxychloride when exposed to sunlight in presence of oxygen.

Phosphorus tribromide, when heated with a current of ozonised oxygen, is converted into phosphorus pentabromide and phosphorous anhydride, and no oxybromide is formed. The same products are obtained when the tribromide is exposed to light in presence of excess of oxygen.

Ozonised oxygen converts arsenic trichloride into arsenic anhydride mixed with a little arsenious anhydride. Oxygen in presence of sunlight, on the other hand, has no action on arsenic trichloride, and ozonised oxygen has no action on cold solutions of phosphorus pentachloride or pentabromide in carbon tetrachloride.

Ozonised oxygen, and oxygen in presence of sunlight, act on solutions of phosphorus diiodide and triiodide in carbon bisulphide at  $-20^\circ$  to  $-5^\circ$ , with liberation of iodine and formation of complex products containing phosphorus, iodine, and oxygen. C. H. B.

### Spontaneous Decomposition of Thiosulphuric acid.

By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1895, **14**, 71—81).—If the spontaneous decomposition of thiosulphuric acid really takes place in accordance with the unimolecular equation  $\text{H}_2\text{S}_2\text{O}_3 = \text{H}_2\text{O} + \text{SO}_2 + \text{S}$ , the rate of the action should be greatest at the outset, when the concentration is at a maximum, but this, at first sight, does not appear to be the case.

The hypothesis proposed by Spring to account for the interval that elapses between the addition of an acid to a solution of a thiosulphate and the consequent precipitation of sulphur, namely, that the sulphur results from the interaction of hydrogen sulphide and sulphurous anhydride produced by secondary action, is untenable, for the precipitation may be effected in the presence of a lead salt without the formation of a trace of lead sulphide.

The only secondary action that might serve to retard the precipitation is that due to the formation of trithionate by the action of liberated sulphurous acid on undecomposed thiosulphate, but this



does not take place to any extent, as the acidity of the product diminishes only very slowly.

The true explanation of the slow appearance of the sulphur is that it is formed from the commencement, but takes time to form visible aggregates. That this is the case is proved by neutralising the mixture of acid and thiosulphate before the formation of any turbidity; the sulphur still appears after the usual interval. The rate of diminution of the thiosulphate also, as determined by iodine titration, steadily diminishes with the time, as required by the unimolecular equation.

The instability of thiosulphuric acid may be accounted for on two hypotheses. According to Ostwald, the hydrogen ions exercise a reducing action on the  $S_2O_3$  ions, whilst, according to the author, it is the undissociated molecules of thiosulphuric acid which split up. If the latter view is correct, the equilibrium between the undecomposed molecules and the free ions must be maintained by the reunion of ions, leading to the retardation and ultimate stoppage of the action at the dilution at which the ions will no longer unite, and the constant  $K$  in the equation  $-dC/dt = KC$  will vary in the same sense as the concentration  $C$ , whilst, if the former view is correct, the constant and the concentration will vary in opposite senses. Actual measurement of the constant at various concentrations show that the two vary in the same sense.

The decomposition of thiosulphuric acid thus takes place in accordance with the equation  $H_2S_2O_3 = H_2O + SO_2 + S$ , in which the undissociated molecules, and not the ions, take part.

The molecular conductivity of sodium thiosulphate is  $\mu_{\infty} = 128$ , from which the velocity of the ion  $S_2O_3/2 = 78.8$ ; Brédig's value, deduced from the conductivity of magnesium thiosulphate, is 91. The molecular conductivity of thiosulphuric acid is  $\mu_{32} = 274.6$ , or of the same order as that of sulphuric acid. JN. W.

**Composition of Extinctive Atmospheres produced by Flames.** By FRANK CLOWES (*Proc. Roy. Soc.*, 1895, 57, 353—357).—Following on the results obtained by mingling gases which are extinctive of flame with air, until a flame burning in the mixed atmosphere was just extinguished (this vol., ii, 443), the author now describes a series of experiments to determine the composition of the atmosphere extinctive of each flame, which is produced by the flame itself when burning in an inclosed volume of air at atmospheric pressure. To obtain trustworthy results, it is necessary that the atmosphere should not be in contact with water, and, moreover, the pressure in the inclosed atmosphere must be constant during the combustion of the flame. For this purpose a bell-jar is employed, the bottom of which dips into a vessel of mercury. The neck is closed by a cork having a U-shaped mercury gauge and a glass tube with a stop-cock. While the flame is burning, the pressure of the air within the bell-jar is maintained uniform by raising or lowering the jar sufficiently to maintain the mercury levels unchanged in the pressure gauge. The composition of the residual atmospheres after the flame has burnt out, agree very fairly with the composition of the artificial

atmospheres consisting of nitrogen and oxygen only, in which the flames are just extinguished when they are inserted.

The author points out that the composition of the extinctive atmosphere produced by the flame of a candle, or of oil or alcohol, which contains 15–16 per cent. of oxygen, 80–81 per cent. of nitrogen, and 3 per cent. of carbonic anhydride, closely corresponds with the average composition of air expired from the lungs. This air can be breathed by most people without producing any distinctly noticeable effect, a result which agrees with the statements made by experienced mining authorities.

The residual atmosphere produced by the hydrogen flame is undoubtedly not respirable, on account of the greatly diminished proportion of oxygen which it contains. The colour of the hydrogen flame undergoes a change of colour from reddish-purple to blue as the proportion of oxygen in the atmosphere is diminished. A similar change is noticed when carbonic anhydride is present in the atmosphere; it is probably due to the lowering of temperature of the flame. All attempts have failed to detect the production of carbonic oxide by this flame, when it is burning in air containing carbonic anhydride.

E. C. R.

**Combination of Nitrogen with Carbon and Sulphur.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 1315–1316).—When electric sparks are passed through a mixture of nitrogen and carbon bisulphide vapour at about 20°, sulphur and carbon are precipitated and the nitrogen is slowly absorbed. A small quantity of mercuric thiocyanate is formed, but the greater part of the nitrogen is converted into more highly condensed products. With the silent discharge in place of sparks, there is no precipitation of carbon, and after some time the nitrogen is completely absorbed. There is no fluorescence such as is observed in the case of argon and benzene. If the product is heated, some carbon bisulphide is regenerated and nitrogen is liberated, but the volume of the latter is much smaller than that of the original gas.

C. H. B.

**Reduction of Nitrous Oxide by Metals in presence of Water.** By PAUL SABATIER and J. B. SENDERENS (*Compt. rend.*, 1895, 120, 1212–1215).—Well-washed nitrous oxide, when allowed to remain in contact with moist iron turnings over mercury, is slowly reduced to nitrogen, some hydrogen being also liberated. An aqueous solution of the gas is also reduced by iron, magnesium, zinc, and cadmium, with production of nitrogen and hydrogen, the latter being derived from the water in presence of the small quantity of ammonia that is formed. No hydrogen is, however, liberated when cadmium is the reducing agent. The iron becomes converted into hydrated ferrous-ferric oxide, which, after being dried, is highly magnetic (compare this vol., ii, 445).

C. H. B.

**Action of Nitric Oxide on Metallic Chlorides.** By V. THOMAS (*Compt. rend.*, 1895, 121, 128–130).—When ferric chloride is subjected to the prolonged action of nitric oxide (see this vol., ii, 271)

at a temperature of 60—100°, and the product is afterwards heated in sealed tubes at about -175°, a red compound,  $5\text{Fe}_2\text{Cl}_4\text{NO}$ , is obtained; this is very hygroscopic, and decomposes very rapidly when exposed to air. When heated in an inert gas, it yields pure ferrous chloride. Another compound,  $\text{Fe}_2\text{Cl}_4\text{NO}$ , with similar properties, is obtained as a brownish-yellow powder by heating ferric chloride in a current of nitric oxide in a porcelain tube to which a long glass tube is attached. The compound sublimes readily and condenses in the glass tube; in composition it is identical with the product of the action of nitrogen oxides on a solution of ferrous chloride at 12.5—25°.

Bismuth chloride rapidly absorbs nitric oxide, and yields a yellow compound,  $\text{BiCl}_3\text{NO}$ ; aluminium chloride is slowly converted into a pale yellow compound,  $\text{Al}_2\text{Cl}_6\text{NO}$ . Both products are extremely hygroscopic and decompose rapidly when exposed to air. When heated in sealed tubes, they melt without decomposing (compare Besson, *Abstr.*, 1889, 834).  
C. H. B.

**Mutual Behaviour of Hydrogen Peroxide and Nitrous acid in very dilute Solutions.** By LUDWIG LOSVAY DE NAGY LOSVA (*Ber.*, 1895, 28, 2031—2032).—The author has arrived at the following conclusions.

1. One part of hydrogen peroxide per million is not completely reduced in acid or neutral solution after remaining in contact with the calculated amount of nitrous acid for 45—50 hours; the greater the excess employed above this quantity, however, the more rapid is the reduction, and when an acid solution containing 15 times, or a neutral solution containing 20 times, the theoretical quantity is employed, hydrogen peroxide can no longer be detected in the liquid.

2. When an acid solution of nitrous acid containing one part per million remains in contact with the calculated amount of hydrogen peroxide for 50—60 hours, it still exhibits feeble indications of the presence of nitrous acid, whilst in neutral solution nitrous acid is easily detected. The rapidity with which oxidation takes place is increased on augmenting the quantity of hydrogen peroxide, but not in any definite proportion. In order to oxidise an acid solution of nitrous acid containing one part per million, vigorous agitation with 800 times the calculated amount of hydrogen peroxide is necessary, a neutral solution requiring 1200 times the theoretical quantity.

3. Direct sunlight accelerates the interaction of hydrogen peroxide and nitrous acid.  
M. O. F.

**Hydrazine Hydrate.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, 14, 85—88).—Hydrazine hydrate boils at 47° (22 mm.); its aqueous solution is very stable, and may be boiled for several hours without undergoing change. The hydrate, however, is slowly decomposed when exposed to air free from carbonic anhydride, and, when confined with oxygen over mercury, is oxidised to nitrogen and water. Hydrazine hydrate dissolves caustic soda and potash and various salts, such as potassium iodide, ammonium sulphate, and barium nitrate, but other salts, such as potassium and zinc sulphates, are not dissolved by it. It dissolves sulphur,

forming an orange-yellow solution, and hence attacks vulcanised india-rubber, ammonium sulphide appearing to be formed. It also appears to dissolve phosphorus. Sodium decomposes hydrazine hydrate, with liberation of hydrogen and ammonia, and the formation of a crystalline compound, possibly  $N_2H_5 \cdot OH$ .

Nearly pure anhydrous hydrazine is obtained as a somewhat viscous liquid when a mixture of the hydrate with excess of barium oxide is distilled under diminished pressure. JN. W.

**Preparation of Hydrazine Hydrate.** By CORNELIUS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 82—84).—Hydrazine vapour does not attack glass at moderate temperatures, so that silver apparatus is unnecessary if the distillations are made under reduced pressure.

In preparing the hydrate from commercial hydrazine sulphate, the latter is first converted into the bromide by means of barium bromide, and this is then decomposed by the theoretical amount of aqueous potash. After the potassium bromide thus formed has been precipitated with alcohol, the alcoholic solution of the hydrate is distilled under the ordinary pressure until the temperature reaches  $108^\circ$ , but little of the hydrate passing over below this point. Any further precipitate of potassium bromide having been removed, the liquid is fractionated first under atmospheric pressure until the temperature reaches  $118^\circ$ , and then under a pressure of 121—122 mm. The higher fractions are dehydrated with barium oxide, by which agent the hydrate is not affected, and the dry hydrate extracted with alcohol. On refractionating the product under a pressure of 121—125 mm., the fraction boiling at  $73^\circ$  contains 99.7 per cent. of hydrazine hydrate, and is free from silica. The yield, however, is only 22 per cent. of that required by theory.

The author adds in a postscript that the use of barium oxide is unnecessary, equally good results having been obtained by simple fractionation. JN. W.

**Reduction of Silica by Carbon.** By HENRI MOISSAN (*Compt. rend.*, 1895, **120**, 1393—1394).—Silica volatilises readily in the electric furnace under the influence of the arc from a current of 1000 amperes and 50 volts (*Abstr.*, 1893, ii, 532), and if the action of the arc is stopped before volatilisation is complete, crystals of silicon, like those described by Senarmont, are sometimes found in the lower part of the crucible. When a mixture of rock crystal and carbon is heated in the electric furnace in a carbon tube closed at one end, the open end of the tube becomes full of flocculent volatilised silica, below which are crystals of carbon silicide, whilst still lower in the tube is a ring of crystals of silicon mixed with some carbon silicide. It follows that silica is reduced to silicon by carbon under the influence of the electric arc. C. H. B.

**Solid Carbonic Anhydride.** By P. VILLARD and R. JARRY (*Compt. rend.*, 1895, **120**, 1413—1416).—Dry carbonic anhydride cooled and solidified in a wide tube melts at  $-56.7^\circ$ , and its vapour

pressure at this temperature is 5.1 atmos.; it resolidifies at the same temperature, and shows the same vapour pressure. These values approximate very closely to those given by Faraday, and practically the same results were obtained with carbonic acid snow prepared in the usual way.

The crystals of carbonic anhydride have no action on polarised light.

The temperature of solid carbonic anhydride under atmospheric pressure is  $-79^{\circ}$ . In making this determination, precautions were taken to protect the thermometer from radiation from surrounding objects. Regnault found  $-78.16^{\circ}$ , and Pouillet  $-79^{\circ}$ ; contrary to the usual statement, the addition of ether does not reduce the temperature, and the minimum of  $-79^{\circ}$  is only obtained when the carbonic anhydride snow is in excess. The heat of dissolution of the solid in the ether is so small that it can only be recognised if the ether has previously been cooled to  $-79^{\circ}$ . Methylic chloride behaves differently, and the solid carbonic anhydride at temperatures below  $-65^{\circ}$  dissolves in it without any evolution of gas, and when the liquid is saturated the temperature is  $-85^{\circ}$ , a result due to the dissolution of the solid. By passing a current of dry air through the mixture its temperature can be reduced to  $-90^{\circ}$ .

Under a pressure of 5 mm., the temperature of the solid anhydride is  $-125^{\circ}$ , and it evaporates very slowly under these conditions. It follows that it should be possible to liquefy oxygen with carbonic anhydride only as the cooling agent and with ordinary laboratory appliances.

C. H. B.

**Gas showing the Spectrum of Helium, the reputed Cause of D<sub>3</sub>, one of the Lines in the Coronal Spectrum.** By WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1895, 58, 65—67), and **Helium, a Gaseous Constituent of Certain Minerals. Part I.** By WILLIAM RAMSAY (*ibid.*, 81—89).—The principal results of these investigations are recorded in the paper by Ramsay, Collie, and Travers (*Trans.*, 1895, 684).

H. C.

**Density of Helium.** By PER T. CLEVE (*Compt. rend.*, 1895, 120, 1212).—The gas obtained from cleveite, freed from hydrogen by passing it over red-hot cupric oxide, and from nitrogen by means of magnesium, had the density 2.02 as compared with hydrogen. It contained no argon.

C. H. B.

**Compound of Argon.** By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 1316—1319).—When a mixture of argon with carbon bisulphide vapour at about  $20^{\circ}$  is subjected to the action of the silent electric discharge, there is no production of fluorescence similar to that observed with argon and benzene, but the argon is gradually absorbed, and if the action of the discharge is prolonged, and the carbon bisulphide is renewed from time to time, the absorption may amount to 56 per cent. of the original volume, and probably would become complete. No product is formed which gives reactions analogous to those of mercuric thiocyanate. When the product is heated

to the boiling point of mercury and up to a dull red heat, argon is liberated in volume equal to about half that originally absorbed. The argon thus set free gives the characteristic green fluorescence when mixed with benzene vapour and subjected to the action of the silent discharge.

C. H. B.

**Constitution of Inorganic Compounds.** By ALFRED WERNER (*Zeit. anorg. Chem.*, 1895, 9, 382—417).—A theoretical paper dealing with salts of oxy-acids and molecular (additive) compounds (compare this vol., ii, 225).

J. B. T.

**Constitution of Metallic Bases.** By NICOLAI KURNAKOFF (*J. pr. Chem.*, 1895, [2], 52, 177—192; compare *Abstr.*, 1894, i, 273).—The author dilates on the necessity for the collation of investigations which have been made into the composition of compounds of the general type,  $MX_m.nA$  (where A is a compound of basic character, or a neutral substance such as water, alcohol, &c.), with a view to the abandonment of the old theory of molecular compounds and the formulation of some system to which such metallic bases may be referred. He then proceeds to discuss the subject under the following heads:—(1) The composition and stability of the metal-ammonia compounds, in which X of the above type is a halogen, and A ammonia. Texts for this portion of the subject are culled from the work of Isambert (*Compt. rend.*, 1880, 91, 768) and of Lachowicz (*Abstr.*, 1889, 569). (2) Changes in the chemical function of both metal and acid in salts induced by the combination of such salts with ammonia or water. (3) The relationship between hydrate and metal-ammonia compounds.

A. G. B.

**Sodamide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1895, 121, 66—69).—Sodamide was obtained as an amorphous, bulky, white, somewhat volatile compound by passing dry ammonia over sodium fused in iron dishes in a glass tube. When exposed to air, it absorbs water, oxygen, and carbonic anhydride, and is converted into a mixture of sodium nitrite, carbonate, and hydroxide. When mixed with water, it yields ammonia and sodium hydroxide, and the reaction develops so much heat that in presence of air the ammonia ignites and violent explosions may be produced. The heat of dissolution is +31.04 Cal. at 20—22°, and hence—

$NH_3$  gas + Na sol. = H gas +  $NH_2$  Na sol.    develops +20.84 Cal.  
 $NH_3$  liq. + Na sol. = H gas +  $NH_2$  Na sol.    „    +16.44 „

The last value would be reduced by 0.5 to 1.0 Cal. if calculated for solid ammonia. It is about 7 Cal. lower than the corresponding value for acetylene, which, in its turn, is 7 Cal. lower than the mean value for the alcohols.

N gas +  $H_2$  gas + Na sol. =  $NH_2$  Na sol. ... develops +33.04 Cal.  
 $NH_3$  Na sol. = H gas +  $NH_2$  Na sol. .... „    +15.64 „

The results obtained by Joannis indicate that solid sodammonium has practically the same heat of formation as solid ammonia, and it

seems probable that the reactions  $\text{NH}_3 \text{ sol.} + \text{Na sol.} = \text{H gas} + \text{NH}_2\text{Na sol.}$  and  $\text{NH}_4 \text{ sol.} + \text{Na sol.} = \text{H gas} + \text{NH}_3\text{Na sol.}$  likewise develop practically the same quantities of heat. It would follow that  $\text{NH}_3 \text{ sol.} + \text{H gas} = \text{NH}_4 \text{ sol.}$  would absorb from  $-15.5$  to  $-16.0$  Cal., and it should not be impossible to realise the conditions necessary to the formation of ammonium. C. H. B.

**Sodium Hyposulphite.** By E. H. EKKER (*Rec. Trav. Chim.*, 1895, **14**, 57—64).—The products of the electrolysis of aqueous solutions of sodium hydrogen sulphite are sodium sulphate, water, and either sodium hydrogen hyposulphite,  $\text{NaHS}_2\text{O}_4$ , or a mixture of sodium hyposulphite and free hyposulphurous acid. The yield, however, is too small to render the method of any practical value for the preparation of the hyposulphites, even when the electrolysis is conducted at a low temperature, and in an atmosphere free from oxygen. The maximum, 41 per cent. of that indicated by theory, was obtained after a current of 1.51 ampère had passed for 30 minutes through a saturated solution of the sulphite, but diminished to 6 per cent. after the lapse of another hour. The diminution of the yield with the time was less marked when the solution was previously rendered alkaline with caustic soda. J. N. W.

**Recovery of Silver from Solutions.** By WILHELM VENATOR (*Chem. Zeit.*, **19**, 1895, 77—78).—The acid solution obtained in the parting of gold is neutralised with potassium carbonate, and then precipitated with potassium chloride. The precipitate is well washed by decantation with hot water to remove any lead, and then made into a paste with brine and mercury, about 10 parts of the latter for 1 part of silver. The silver is now reduced by the introduction of scraps of iron, and it then rapidly amalgamates with the mercury. Five hundred grams of silver chloride is generally reduced in 10 hours. The amalgam is cleansed by washing with hot water, and freed from excess of mercury by pressing it in a linen bag, and finally heated in a retort to recover the mercury. As the residue, however, still retains mercury, sometimes as much as 1 per cent., the metal must be purified by fusion with borax.

Potassium nitrate is obtained as a bye-product.

L. DE K.

**Basic Halogen Salts of the Alkali Earths.** By TASSILLY (*Compt. rend.*, 1895, **120**, 1338—1340).—*Strontium oxybromide*,  $\text{SrBr}_2 \cdot \text{SrO} + 9\text{H}_2\text{O}$ , is obtained in beautiful prisms by boiling the oxide with a concentrated solution of the bromide. It is not hygroscopic, but is decomposed by carbonic anhydride and by water. The basic iodide,  $2\text{SrI}_2 \cdot 5\text{SrO} + 30\text{H}_2\text{O}$ , is obtained in slender needles by dissolving 100 grams of strontium iodide in 100 c.c. of a cold saturated solution of the hydroxide, and boiling until the volume of the liquid is reduced to about one-third. The basic iodide differs considerably from the basic chloride and bromide, and in this respect strontium differs from calcium (this vol., ii, 45).

The barium oxybromide and oxyiodide which Beckmann obtained mixed with the hydroxide are obtained pure in the following ways.

Thirty parts of finely powdered barium hydroxide are added to a hot solution of 300 parts of the bromide in 330 parts of water, and the mixture is heated and allowed to cool; slender, silky needles separate, which have the composition  $\text{BaBr}_2 \cdot \text{BaO} + 5\text{H}_2\text{O}$ . The oxyiodide is obtained in colourless, highly refractive prisms of the composition  $\text{BaI}_2 \cdot \text{BaO} + 9\text{H}_2\text{O}$ , by dissolving barium iodide in its own weight of a cold saturated solution of the hydroxide, and boiling until the volume of the liquid is reduced to one-third. C. H. B.

**Molecular Changes in Chromium Hydroxide.** By ALBERT RECOURA (*Compt. rend.*, 1895, **120**, 1335—1338).—The author has previously shown that the precipitate produced by alkali hydroxides in green solutions of chromium salts has the composition  $\text{Cr}_2\text{O}(\text{OH})_4$  (Abstr., 1894, ii, 382), and reacts with 4 mols. HCl only, whereas the normal hydroxide reacts with 6 mols. HCl. He now finds that when chromium hydroxide is dissolved in solutions of alkali hydroxides and reprecipitated by neutralisation with an acid, the power of the precipitate to combine with acids diminishes as the time that it has remained in the alkaline solution increases. After 10 minutes, the precipitate reacts with only 3 mols. HCl, and further addition of acid produces no thermal disturbance. After about three hours, the precipitate reacts with only 1 mol. HCl, in which, however, it dissolves immediately and completely. After a longer time, the combining power diminishes still further, and the precipitate can no longer be completely dissolved in the acid at the ordinary temperature, and finally, after remaining about two months in the alkaline solution, the precipitate will not redissolve in acid at all. It would seem that the alkali exercises a progressive dehydrating effect on the hydroxide  $\text{Cr}_2(\text{OH})_6 + \text{Aq}$ , anhydrides being formed by the gradual elimination of OH-groups, and the final product being  $\text{Cr}_2\text{O}_3 + \text{Aq}$ . C. H. B.

**Molybdenum.** By HENRI MOISSAN (*Compt. rend.*, 1895, **120**, 1320—1326).—Molybdenum dioxide, prepared by strongly heating ammonium molybdate, is mixed with one-tenth of its weight of sugar carbon, and heated for about six minutes in a carbon crucible in an arc produced by a current of 800 ampères and 60 volts. With the proportions given, the molybdenum oxide is in excess, and if the action of the arc is stopped before the outer portions of the mixture in contact with the crucible have had time to fuse, molybdenum is obtained quite free from carbon, and containing only from 0.1 to 0.2 per cent. of slag as an impurity (compare Abstr., 1893, ii, 471). If, however, the action of the arc is prolonged until the whole mixture fuses, the crucible is attacked, and, on cooling, a hard, brittle ingot of carboniferous molybdenum is obtained. If the proportion of carbon is 2.5 to 3.0 per cent., the metal is white and very hard, and has all the properties of the molybdenum described by Debray; if the proportion is 4.9 to 5.5 per cent., the metal is grey, and is sufficiently hard to scratch steel and quartz, but is very mobile when fused, and is readily cast in ingots of 8 to 10 kilos. The fused metal dissolves carbon rapidly, and, on cooling, the latter separates as



graphite, but if the metal is saturated with carbon, a crystalline carbide is formed.

*Molybdenum carbide*,  $\text{Mo}_2\text{C}$ , is best obtained by heating a mixture of molybdenum dioxide with one-fifth its weight of carbon for eight or ten minutes in a carbon crucible in an arc formed by a current of 800 ampères and 50 volts. Any excess of carbon remains mixed with the product in the form of graphite. The carbide shows a brilliant, white, crystalline fracture, cleaves readily, and seems to crystallise in elongated prisms; sp. gr. = 8.9.

Pure fused molybdenum is as malleable as iron, files and polishes readily, and will not scratch glass or rock crystal; sp. gr. = 9.01. It can be forged when hot. If free from carbon and silicon, it oxidises but little in air below a red heat, and remains unchanged for several days in water, even when the latter contains carbonic anhydride. At a dull red heat, molybdenum oxidises superficially in the air, and at  $600^\circ$  oxidation becomes marked, and molybdic anhydride slowly volatilises. The anhydride is the product of oxidation in air at high temperatures, but is accompanied by a blue oxide in the oxy-hydrogen flame.

Fused potassium chlorate attacks the metal violently, and the nitrate also oxidises it rapidly, although less violently than the chlorate. If a mixture of molybdenum and lead peroxide is heated, there is intense development of light and heat.

Sulphur has no action on molybdenum at  $440^\circ$ , but hydrogen sulphide at  $1200^\circ$  converts the metal into a sulphide closely resembling molybdenite. Fluorine has no action on masses of the metal at ordinary temperatures, but acts on the coarsely powdered metal with incandescence and formation of a volatile fluoride. Silver, zinc, and lead fluorides are decomposed when heated with molybdenum, but no volatile fluoride is formed. Chlorine attacks molybdenum at a dull red heat without incandescence, and bromine combines with it, though not energetically, at a cherry-red heat. Iodine has no action at the softening point of glass. When the metal is gently heated with phosphorus pentachloride, a volatile chloride is formed, which rapidly acquires a beautiful blue colour when exposed to moist air. This reaction is obtained with most molybdenum compounds, and constitutes a ready test for the metal.

The action of halogen acids on pure molybdenum is similar to their action on the fused metal as described by Berzelius, Debray, and others. Hydrogen fluoride is without effect, except in presence of nitric acid, when the metal is rapidly attacked.

Pure molybdenum does not combine with nitrogen at  $1200^\circ$ , nor with phosphorus at the melting point of glass, but when heated with boron in the electric furnace, it forms a boride, which crystallises in iron-grey, prismatic needles. With silicon, under similar conditions, it forms a crystalline silicide, which does not melt in the oxy-hydrogen flame.

When pure molybdenum is heated in carbon at about  $1500^\circ$ , it undergoes cementation and becomes hard enough to scratch glass, and if heated at  $300^\circ$  and suddenly cooled in water, it becomes brittle and will scratch rock crystal. On the other hand, when

carboniferous molybdenum is heated with the dioxide at a temperature much below its melting point, the carbon is removed, a result which seems to be due to the volatility of the oxide.

Molybdenum in masses may be used as a deoxidising agent for overblown Bessemer steel, and has the advantage that the oxide produced is volatile, and any excess of metal that may remain with the iron is malleable like the latter, and will acquire temper under the same conditions.

C. H. B.

**Ammonium Sodium Hydrogen Tungstates.** By L. A. HALLOPEAU (*Compt. rend.*, 1895, **120**, 1343—1345).—When excess of ammonia is added drop by drop to a cold and somewhat dilute solution of sodium paratungstate, an abundant crystalline precipitate is formed, and when this is dissolved in warm water and the solution evaporated in a vacuum, a small quantity of crystals of the salt  $16\text{WO}_3, 3\text{Na}_2\text{O}, 3(\text{NH}_4)_2\text{O} + 22\text{H}_2\text{O}$  is obtained; it loses 15 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ . The mother liquor, on further concentration, deposits a considerable quantity of somewhat bulky, colourless, transparent, flattened prisms of the salt  $12\text{WO}_3, 4\text{Na}_2\text{O}, (\text{NH}_4)_2\text{O} + 25\text{H}_2\text{O}$ ; it loses 19 mols.  $\text{H}_2\text{O}$  at  $100^\circ$ . The first salt is analogous to the salt  $8\text{WO}_3, 3(\text{NH}_4)_2\text{O} + 8\text{H}_2\text{O}$ , described by Marignac and by Laurent; the second belongs to the series of ammonium sodium paratungstates which have been described by Marignac, Knorre, and Gibbs.

C. H. B.

**Paratungstic acid.** By L. A. HALLOPEAU (*Compt. rend.*, 1895, **121**, 61—63).—Paratungstic acid is not readily obtained by the action of hydrogen sulphide on the lead salt, nor of hydrochloric acid on the mercurous salt, and although a pure solution of the acid is formed when the silver salt is decomposed by hydrochloric acid, the silver chloride is difficult to separate. The best method is to mix barium paratungstate with a quantity of dilute sulphuric acid not quite sufficient for complete decomposition.

Dilute solutions of paratungstic acid are not decomposed by heat, but prolonged boiling partially converts the paratungstic into metatungstic acid. When the solution is evaporated, even in a vacuum, at the ordinary temperature, some tungstic acid is formed. Alkalis neutralise the solution, and yield paratungstates. Hydrochloric, nitric, and sulphuric acids decompose dilute solutions of paratungstic acid; hydrogen sulphide reduces them with formation of the blue or the green oxide; acetic, phosphoric, and carbonic acids have no action. Organic substances, including filter-paper, reduce the acid with formation of the blue oxide, and a solution mixed with alcohol is similarly reduced when exposed to light.

There would seem to be no doubt that paratungstic acid can exist in the free state in aqueous solution.

C. H. B.

**Action of Heat on Iridium Potassium Nitrites.** By ALEXANDRE JOLY and ÉMILE LEIDIE (*Compt. rend.*, 1895, **120**, 1341—1343).—Iridium potassium nitrite is best prepared by adding sodium nitrite to a hot and slightly acid solution of sodium iridiochloride until it is decolorised, boiling to expel nitrous oxides, and adding excess of

potassium chloride. The white precipitate is thoroughly washed, and dried at 100—105°. The salt begins to decompose at about 300°, and decomposition is slow and incomplete at 360°, but becomes rapid at 440°. When it is heated in a vacuum at 440°, nitrogen and nitric oxide are liberated, and a greenish-black powder is left. When this is treated with water, potassium nitrite, nitrate, and chloride (present as an impurity) dissolve, and after a time a deep brown, colloidal product dissolves, and a very heavy, black powder is left. The former consists of hydrated iridium dioxide, quite free from alkali, and can be precipitated by adding ammonium chloride; the latter has very nearly the composition  $6\text{IrO}_2, \text{K}_2\text{O}$ , and seems to be the potassium salt of *hexairidious acid*,  $(\text{IrO})_6\text{O}_5(\text{OH})_2$  or  $6\text{IrO}(\text{OH})_2 - 5\text{H}_2\text{O}$ . This view is supported by the composition of the gas liberated when the double nitrite is heated.

If the double nitrite is heated at incipient redness in a muffle and the product is thoroughly washed, the residue has the composition  $12\text{IrO}_2, \text{K}_2\text{O}$ , and seems to be the potassium salt of *dodecairidious acid*,  $(\text{IrO})_2\text{O}_{11}(\text{OH})_2$  or  $12\text{IrO}(\text{OH})_2 - 11\text{H}_2\text{O}$ .

C. H. B.

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## Mineralogical Chemistry.

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**Graphitite from Monte Pisano.** By FAUSTO SESTINI (*Gazzetta*, 1895, **25**, i, 121—126; compare this vol., ii, 400).—Two minerals from Monte Pisano were found to be samples of graphitite by Luzi's test (Abstr., 1893, ii, 320); the following analytical results were obtained.

	H <sub>2</sub> O (hygroscopic).	H <sub>2</sub> and H <sub>2</sub> O (combined).	Carbon.	Residue on heating.
I .....	5.52	2.65	48.88	42.95
II .....	1.95	1.83	18.67	77.55

W. J. P.

**Sylvanite from Stassfurt.** By W. SCHIMPF (Zeit. Kryst. Min., 1895, **25**, 92—93).—The sample examined is of interest as containing in negative crystals a relatively large amount of hydrogen sulphide, which gas, on dissolving the salt, escapes under pressure with a crackling noise; hence the name "knistersalz" applied to it. There are also larger cavities containing air and perhaps other gases; and others inclosing mother liquor, to which is attributed the impurities shown in the analysis. The hydrogen sulphide amounts to 3.01 per cent. by volume.

KCl.	NaCl.	MgCl <sub>2</sub> .	CaSO <sub>4</sub> .	H <sub>2</sub> S.	Insoluble.	Loss on fusion.	Total
99.2390	0.2420	0.0890	0.0730	0.0023	0.1080	0.2847	100.0331

L. J. S.

**Copper Iodide (Marshallite) from Broken Hill, N.S.W.** By C. W. MARSH (*Journ. and Proc. Roy. Soc. N.S.W.*, 1892, **26**, 326—329).—This new mineral occurs as small, translucent, reddish-brown crystals on cerussite; the crystal form is given as tetragonal-

hemihedral (compare, however, H. A. Miers, *Zeit. Kryst. Min.*, 1894, **24**, 207, who gives it as cubic and tetartohedral); streak orange-yellow. When heated, it gives off iodine, and it is soluble in hot nitric acid with evolution of iodine. The name Marshite is proposed by A. Liversidge.

L. J. S.

**Cadmiferous Blende from Mies: Rhodochrosite from Asia Minor.** By HEINRICH VON FOULLON (*Zeit. Kryst. Min.*, 1895, **24**, 642—643; from *Verh. k. k. geol. Reichsanst.*, 1892, 171).—(1) The occurrence of a bright yellow coating on quartz which, on analysis, was found to consist of cadmium sulphide (greenockite) led to the determination of the amount of cadmium in the blende of Mies, Bohemia; analysis gave

Cd.	Cu.	Pb.	Zn.	Fe.	S.	SiO <sub>2</sub> .	Total.
0·64	0·18	0·04	62·76	1·79	32·42	1·60	99·43

(2) Rhodochrosite, occurring as large rhombohedra with galena, blende, fahlerz, &c., at the Ary Maghara mine, near Balia-Maaden, gave on analysis

MnO.	MgO.	FeO.	CaO.	
19·67	4·62	0·74	32·05	L. J. S.

**Thallium and Molybdenum in Hæmatite.** By LARS J. IJELSTRÖM (*Zeit. Kryst. Min.*, 1895, **25**, 94).—In a specimen of platy hæmatite from the Sjö mine, Örebro, Sweden, molybdenum was found, which “as Mo<sub>2</sub>O<sub>3</sub> (up to 9 per cent.) possibly occurs as isomorphously mixed with Fe<sub>2</sub>O<sub>3</sub>.” The hydrogen sulphide precipitate obtained from a massive specimen contained molybdenum, calcium and thallium as shown by the spectroscope; another sample contained molybdenum but no thallium.

L. J. S.

**Baddeleyite (Native Zirconia).** By LAZARUS FLETCHER (*Min. Mag.*, 1893, **10**, 148—160).—The characters of this new mineral were determined on a single, rough crystal from Rakwana, Ceylon, where it was found with geikielite. The crystal is opaque, and of an iron-black colour, and submetallic to subresinous in lustre; it is monosymmetric, and twinned on the ortho-pinacoid. Thin splinters are transparent and pleochroic; plane of the optic axes the plane of symmetry. Before the blowpipe, it is incandescent and infusible; insoluble in acids. The chemical examination on small splinters showed the mineral to consist of zirconia. Sp. gr. 6·025. The same mineral from Brazil has been described by E. Hussak under the name “brazilite” (*Jahrb. f. Min.*, 1892, ii, 141), its true chemical nature not, however, being published until later (compare Abstr., 1893, ii, 286). Recently the same author has re-described the mineral under the name baddeleyite (*Tsch. Min. Mitth.*, 1895, **14**, 395), the only discrepancy between this description and that of the Ceylon crystal being in the density and cleavage.

L. J. S.

**Celestite from Giershagen, Westphalia.** By ANDREAS ARZRUNI and KONSTANTIN THADDÉE ( *Zeit. Kryst. Min.*, 1895, **25**,

38—72).—The celestite from this locality is of interest as being chemically pure strontium sulphate, neither calcium nor barium being detected spectroscopically. The crystals are prismatic in the direction of the *c* axis, and are mostly colourless;  $a:b:c = 0.77962:1:1.28533$ . Sp. gr. 3.9665. The mean of four determinations gave  $\text{SO}_3 = 43.71$  per cent., there being only a slight variation; the results for the amount of strontium, however, varied with the method of analysis, and it is shown that greater accuracy is obtained when it is precipitated as carbonate than as sulphate; but that the best results are obtained when the mineral is decomposed with a saturated solution of ammonium carbonate. The variations in the crystal angles of celestite are discussed in detail, and it is pointed out that this variation, of  $1^\circ$  or more, which is usually considered (but not at all proved) to be due to the presence of calcium or barium, occurs not only on crystals from different localities but even on the same crystal. The cause of this variation is explained by the crystals being built up of smaller elements not quite in parallel position, the influence of any isomorphously contained calcium, &c., being quite subordinate. The variations of the optic axial angle and of the sp. gr. are more likely to be due to the presence of calcium, &c., although no connection has been traced; the not quite parallel growth will, however, have some influence on the optic axial angle. From the published measurements, the following constants for "normal" celestite are deduced.  $a:b:c = 0.78093:1:1.28324$ .  $2V_{\text{ana}} = 50^\circ 34'$ ,  $2E = 87^\circ 45'$ . Sp. gr. 3.9665.

The existence of barytocelestite as a true isomorphous mixture is doubted. L. J. S.

**Kamarezite.** By KARL H. E. G. BUSZ (*Jahrb. f. Min.*, 1895, i, 115—119).—This new mineral from Kamareza, Laurium, Greece, is grass-green and shows a crystalline structure, with small, needle-shaped, apparently orthorhombic crystals in cavities. The mean of four partial analyses is

CuO.	FeO.	SO <sub>3</sub> .	H <sub>2</sub> O. [diff.]
51.50	0.69	17.52	[30.29]

This agrees with the formula  $3\text{CuO}, \text{SO}_3, 8\text{H}_2\text{O}$ . About half the water is given off between  $220^\circ$  and a low red heat; at a higher temperature, the remainder of the water and some sulphuric anhydride are expelled, the residue being black, and consisting of sulphide and oxide of copper. Sp. gr. 3.98. L. J. S.

**A Basic Ferric Sulphate.** By ARTHUR H. CHURCH (*Min. Mag.*, 1895, 11, 13—14).—An orange-coloured ochreous substance from Parys Mount, Anglesey, which under the microscope was seen to be crystalline, gave on analysis

SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> , CaO, &c. [Diff.]
13.44	57.85	2.14	26.36	[0.21]

Half the water was lost at  $100^\circ$ . This agrees with the formula

$2\text{Fe}_2\text{O}_3, \text{SO}_3, 8\text{H}_2\text{O}$ . The yellow precipitate produced on exposing ferrous sulphate solution to the air corresponds with this.

L. J. S.

**Angelite.** By GEORGE T. PRIOR and LEONARD J. SPENCER (*Min. Mag.*, 1895, 11, 16—23).—This rare mineral, before only known in the massive state, was found as colourless, transparent, mono-symmetric crystals with bournonite from Machacamarca, Bolivia. Analysis gave

$\text{P}_2\text{O}_5$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{H}_2\text{O}$ .	Total.
34·60	51·40	0·11	13·77	99·88

this agreeing with the formula  $2\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, 3\text{H}_2\text{O}$ . Sp. gr. 2·696.

L. J. S.

**Analyses of some Arsenates and Phosphates.** By ARTHUR H. CHURCH (*Min. Mag.*, 1895, 11, 1—12).—(1.) Euchroite, a specimen from Libethen, Hungary, of sp. gr., 3·42, gave, on analysis,

$\text{H}_2\text{O}$ in a vacuum.	$\text{H}_2\text{O}$ at $100^\circ$ .	$\text{H}_2\text{O}$ at low redness.	$\text{CuO}$ .	$\text{As}_2\text{O}_5$ .	$\text{P}_2\text{O}_5$ .	Unde- termined.
1·22	1·90	16·16	47·26	30·90	1·48	1·08

This agrees with the usually accepted formula  $4\text{CuO}, \text{As}_2\text{O}_5, 7\text{H}_2\text{O}$ . The water lost in a vacuum and at  $100^\circ$  corresponds with  $1\text{H}_2\text{O}$ .

(2.) Liroconite. A Cornish specimen of sp. gr. 2·97 gave on partial analysis

$\text{H}_2\text{O}$ in a vacuum.	$\text{H}_2\text{O}$ at $100^\circ$ .	$\text{CuO}$ .	$\text{As}_2\text{O}_5$ .	$\text{P}_2\text{O}_5$ .
6·40	9·85	36·73	23·85	1·02

This corresponds with a loss of  $3\text{H}_2\text{O}$  in a vacuum and of  $5\text{H}_2\text{O}$  at  $100^\circ$ , and with the formula  $4\text{CuO}, \text{Al}_2\text{O}_3, \text{As}_2\text{O}_5, 13\text{H}_2\text{O}$ .

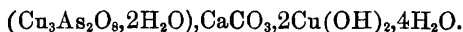
(3.) Clinoclase. Analysis gave

$\text{H}_2\text{O}$ . [Diff.] [7·20]	$\text{CuO}$ .	$\text{As}_2\text{O}_5$ .
	62·72	30·08

Formula  $3\text{CuO}, \text{As}_2\text{O}_5, 3(\text{CuO}, \text{H}_2\text{O})$ . Only 0·08 per cent. of water was lost in a vacuum and at  $100^\circ$ . A trace of phosphoric acid was present.

(4.) Tyrolite. In a previous paper (this Journal, 1873, 26, 108) the author considered the calcium carbonate in this mineral to be present as an essential ingredient and not as an accidental impurity, and the following experiment is taken to support this view. A current of carbonic anhydride, passed through water in which the powder was suspended, acted on the mineral as a whole, the solution containing the same relative amounts of calcium and copper as the original mineral; further on allowing the solution to remain for a time a substance separated on the surface having all the appearances of the original mineral. The absence of carbonic anhydride in the Utah mineral analysed by Hillebrand is explained by the mineral not being tyrolite, or to elimination by substitution. In the analyses given in the

paper quoted the 7 or 8 per cent. of water lost in a vacuum or at  $100^{\circ}$  is now considered as essential, and, as it represents half the total water, these analyses are now interpreted as

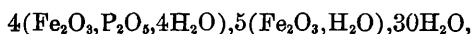


(5.) Pharmacolite. In a vacuum at  $16^{\circ}$ , there was a loss corresponding with  $3\text{H}_2\text{O}$  in the formula  $2\text{CaO}, \text{H}_2\text{O}, \text{As}_2\text{O}_5, 5\text{Aq}$ ; between  $100^{\circ}$  and  $200^{\circ}$  there was a further loss corresponding with  $1\text{H}_2\text{O}$ .

(6.) Cacozenite. Analysis of a Bohemian specimen gave

$\text{H}_2\text{O}$ in a vacuum.	$\text{H}_2\text{O}$ on ignition.	$\text{Fe}_2\text{O}_3$ .	$\text{P}_2\text{O}_5$ .	F.
18.69	13.11	48.57	19.76	trace

From this, the formula  $9\text{Fe}_2\text{O}_3, 4\text{P}_2\text{O}_5, 51\text{H}_2\text{O}$  is deduced, or



or  $(\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, 3\text{H}_2\text{O}), (\text{Fe}_2\text{O}_3, 2\text{H}_2\text{O}), 7\text{H}_2\text{O}$ .

The  $30\text{H}_2\text{O}$  in the second formula corresponds with the water lost in a vacuum over sulphuric acid.

(7.) Kühnrite. Analysis of a specimen from Långban gave

$\text{CaO}$ .	$\text{MgO}$ .	$\text{MnO}$ .	$\text{As}_2\text{O}_5$ .	Total.
21.61	13.00	3.28	56.25	94.14

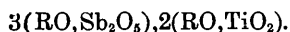
The main part of the deficiency is due to an intimate admixture of about 7 per cent. of calcite with the true kühnrite,  $(\text{Ca}, \text{Mg}, \text{Mn})_3\text{As}_2\text{O}_8$ . At a low redness there was a loss of only 0.26 per cent.

L. J. S.

**Lewisite and Zirkelite, two new Brazilian Minerals.** By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1895, 11, 80—88). —*Lewisite* occurs at the cinnabar mine of Tripuhy, near Ouro Preto, as small, translucent, regular octahedra of a honey-yellow to colophony-brown colour, and vitreous to resinous lustre. It has a fairly perfect octahedral cleavage; sp. gr. 4.950. Insoluble in acids. Analysis gave

$\text{Sb}_2\text{O}_5$ .	$\text{TiO}_2$ .	$\text{CaO}$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{Na}_2\text{O}$ .	Total.
67.52	11.35	15.93	4.55	0.38	0.99	100.72

This agrees with the formula,  $5\text{RO}, 3\text{Sb}_2\text{O}_5, 2\text{TiO}_2$ , or



The mineral is thus related on one side to the calcium titanate perovskite, and on the other to the calcium antimonates, atopite and romeite; or it is related to the pyrochlore group in having antimonic acid in place of niobic acid.

A new titanioantimonate of iron, apparently orthorhombic, containing about 40 per cent. of  $\text{FeO}$  and about 17 per cent. of  $\text{TiO}_2$ , and with sp. gr. 4.529, is mentioned as being found at the same locality. Several of the associated minerals are described crystallographically.

*Zirkelite*, this new calcium zirconate and titanate occurs at the



iron mine of Jacupiranga, S. Paulo, as small, opaque, regular octahedra, black and of a resinous lustre; sp. gr. 4·706. Analysis gave

ZrO <sub>2</sub> .	TiO <sub>2</sub> .	FeO.	CaO.	MgO.	Loss.	Total.
48·90	30·89	6·64	11·61	0·49	1·02	99·55

The relative amounts of ZrO<sub>2</sub> and TiO<sub>2</sub> are somewhat uncertain, owing to the difficulty of separation. L. J. S.

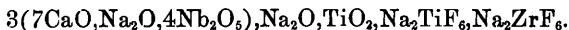
**Pyrochlore from Alnö, Sweden.** By P. J. HOLMQUIST (*Jahrb. f. Min.*, 1895, ii, Ref. 15—16; from *Geol. För. Förh.*, 1893, **15**, 588—606).—Numerous octahedra of this mineral occur with zircon, perovskite, titaniferous magnetite and other minerals in a metamorphic limestone at the above locality; the larger crystals are light-brown to black, and have a sp. gr. of 4·3528—4·3533 (Analysis I), whilst the smaller crystals are transparent, and of a light, reddish-yellow colour, having a sp. gr. of 4·4460 (II). In sections, the mineral is fresh and isotropic, and shows a zonal structure.

	Nb <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	ZrO <sub>2</sub> .	FeO.	Ce <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.
I.	58·83	3·70	2·90	4·20	3·99	0·41	16·75	3·44	1·41
II.	63·64	—	4·90	1·14	4·36	—	18·13	4·99	0·60
	H <sub>2</sub> O.	F.	Total.	Total (less O for F <sub>2</sub> ).					
I.	0·78	4·34	100·75	98·92					
II.	0·47	4·31	102·54	100·73					

These analyses may be represented by the general formula  $m(2\text{RO}, \text{Nb}_2\text{O}_5) + \text{RO}, (\text{Zr}, \text{Ti})\text{O}_2$ . In II there is enough fluorine to replace all the oxygen in the metazirconate, and  $m = 6$ , so that the formula becomes  $6(2\text{RO}, \text{Nb}_2\text{O}_5) + \text{RZrF}_6$ , or



For I, if Ti : Zr = 2 : 1, the formula may be written



As the fluorine and alkalis of pyrochlore and other minerals exist in the atomic ratio of 1 : 1, it is suggested by the author that in the action of alkaline fluorides as mineralising agents, the alkalis as well as the fluorine go to form the resulting minerals. L. J. S.

**Geikielite.** By ALLAN B. DICK (*Min. Mag.*, 1893, **10**, 145—147).—This new mineral was found as pebbles in the gem mines of Rakwana, Ceylon. It is bluish- or brownish-black, and in thin fragments, by transmittent light, purplish-red; there is one perfect cleavage with an imperfect one nearly at right angles to the former; the lustre on the cleavage face is metallic-adamantine. Optically uniaxial. It is infusible, and is decomposed by hot, concentrated hydrochloric acid, and also by cold hydrofluoric acid, the titanium oxide separating out. Analysis gave

TiO <sub>2</sub> .	MgO.	FeO.	Total.
67·74	28·73	3·81	100·48

This mineral  $\text{MgTiO}_3$ , corresponds to the calcium titanate, perovskite. Sp. gr., 3·98—4. Some of the pebbles inclose much rutile.

L. J. S.

**Nephrite from Kuen-Lun.** By ANDREAS ARZRUNI (*Zeit. Kryst. Min.*, 1895, **24**, 632; from *Zeit. f. Ethnologie, Berlin*, 1892, 19).—A specimen of marked schistose and fibrous texture, from the old locality Shahidulla-Chodja, showed under the microscope secondary serpentine and a chloritic mineral, also isolated prisms of pyroxene partly altered to amphibole, and large amphibole crystals, around which the nephrite fibres were arranged perpendicularly. Analysis gave results in agreement with the usual metasilicate formula.

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.
57·81	1·58	2·60	13·71	22·51	1·75	99·96

To the east of the old localities, nephrite has recently been found, namely between Kukunor and the Nan-Schan mountains, in the Chinese province Kansu.

L. J. S.

**Analyses of Heulandite and Smithsonite.** By L. G. EAKINS and HENRY N. STOKES (*Zeit. Kryst. Min.*, 1895, **24**, 624; from *Bull. U.S. Geol. Survey*, 1892, No. **90**, 62).—Heulandite from Anthracite Creek, Gunnison Co., Colorado, gave

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.	Sp. gr.
57·38	17·18	8·07	0·40	0·82	16·27	100·12	2·24

Smithsonite, of a bright golden-yellow colour, from Marion Co., Arkansas, gave

$\text{CO}_2$ .	$\text{ZnO}$ .	$\text{CdO}$ .	$\text{CaO}$ .	$\text{FeO}$ .	$\text{CdS}$ .	$\text{SiO}_2$ .	Total.
34·68	64·12	0·63	0·38	0·14	0·25	0·06	100·26

L. J. S.

**Analyses of Natrolite, Tourmaline, Spessartite, Bismuthinite, and Felspar.** By WILLIAM H. MELVILLE (*Zeit. Kryst. Min.*, 1895, **24**, 622—623; from *Bull. U.S. Geol. Survey*, 1892, **90**, 38 and 65).—(1) Natrolite from Magnet Cove, Arkansas, gave, on analysis,

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
47·56	26·82	0·20	0·13	0·09	15·40	9·63	99·83

Of the water 0·07 per cent. was given off at  $100^\circ$ , 0·19 at  $250^\circ$ , 3·42, at  $300$ — $350^\circ$ , and 5·95 on ignition. Sp. gr. 2·261.

(2) Tourmaline, occurring at Colfax, Nevada Co., California, as transparent, almost colourless needles, gave

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	F.	Loss at $100^\circ$ .
36·40	33·64	3·13	1·51	10·01	0·12	2·49	0·74	0·02

Loss on ignition.	$\text{B}_2\text{O}_3$ .	Total.	Total (less O for F).	Sp. gr.
3·51	6·52	98·07	97·76	3·065

(3) Spessartite, from Llano Co., Texas, gave

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	Alkalis.	Loss.	Total.
35.93	18.08	4.60	31.77	8.48	0.69	0.17	0.39	100.38

To bring this into agreement with the garnet formula, some of the manganese must exist as sesquioxide.

(4) Bismuthinite, from Rosario District, Sinaloa, Mexico, gave

Bi.	Pb.	Cu.	Fe.	S.	SiO <sub>2</sub> .	Total.
72.90	6.03	1.67	0.35	18.11	0.63	99.69

This analysis indicates admixture of galena, copper pyrites and quartz with the bismuth sulphide. The mineral occurs, as a large deposit, in large, brilliant blades, and is used for extraction of bismuth, as well as of gold and silver. Sp. gr. 6.624.

(5) Felspar, from the elaeolite-syenite of Litchfield, Maine, gave

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	65.14	18.19	0.25	0.33	0.16	14.14	1.68	0.17	100.06
II.	68.28	19.62	0.23	0.31	0.09	0.39	10.81	0.09	99.82

Sp. gr. of I, 2.56; of II, 2.622.

L. J. S.

**Composition of Idocrase (Vesuvian).** By MATS WEIBULL (*Zeit. Kryst. Min.*, 1895, **25**, 1—37).—The mode of occurrence and the crystallography of brown idocrase from Tennberget, Dalarne, Sweden, are minutely described. The mean of six partial analyses is given under I; sp. gr. 3.325;  $a:c = 1:0.53539$ ; optically uniaxial and negative. The orthosilicate formula,  $12\text{CaO}, 3\text{Al}_2\text{O}_3, 10\text{SiO}_2, (\text{H}_2\text{O}, \text{F}_2)$ , is deduced, the alkalis being reckoned as  $\text{R}''\text{O}$ . The loss on ignition is slightly greater than  $\text{H}_2\text{O} + \text{F}$ , and experiments were made which tend to show that the white fumes evolved on ignition consist of aluminium fluoride.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	B <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MnO.	MgO.	
I.	37.83	16.92	—	1.78	3.36	35.01	0.06	2.20	
II.	37.97	16.25	0.10	3.87	0.55	35.34	—	2.46	
	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.		F.	Total.	Total (O less F).		
I.	0.23	1.15	0.77		1.72	101.03	100.30		
II.	0.13	0.28	1.08 1.60		—	99.63	—		

Previous analyses, in which the water and fluorine were directly determined, are reduced to the above formula. A structural formula showing the relation to garnet is given.

Some idocrases free from fluorine have also been examined; crystals from Cziklowa, Hungary, with  $a:c = 1:0.5340$ , and showing optical anomalies, gave the analysis II. This analysis agrees with the above formula when the water is considered as partly an acid and partly a basic constituent; this is supported by the fact that part of the water

(1.08 per cent.) goes off at a red heat, whilst the remainder is only expelled at a much higher temperature; the former part being considered to be the basic, and the latter the acid water. Previous analyses of idocrases free from fluorine are discussed, and in the formula of some, the radicles  $\text{Al}(\text{OH})$ ,  $\text{Mg}(\text{OH})$  or  $\text{Ca}(\text{OH})$  are supposed to exist with the bases. It is noticed, that although the amounts of the other bases vary, the calcium is pretty constant (35 per cent.), this represents five-sixths  $\text{R}''$ , and in the general formula  $\text{Ca}_5\text{R}''\text{Al}_2[\text{R}'''(\text{OH}, \text{F})]\text{Si}_5\text{O}_{20}$ . No connection can be traced between the variation of the ratio  $a : c$  and the chemical composition.

L. J. S.

**Zinnwaldite from Mourne Mountains, Co. Down.** By WILLIAM J. SOLLAS (*Proc. Roy. Irish Acad.*, 1890, [3], 1, 379—380).—This lithia mica occurs as well-developed crystals with topaz, &c., in the druses of the Mourne Mountain granite. The crystals show a zonal structure, the centre being usually green, this graduating to colourless at the periphery; this difference in colour is associated with a difference in specific gravity, of 3.2 to 2.8 (the less dense portion being lighter in colour, and containing more lithium), and an increase in the optic axial angle from  $44^\circ 4'$  to  $52^\circ 6'$ . These variations indicate a passage from a mica richer in iron and magnesia at the centre to one richer in alumina and alkalis at the periphery; this difference in composition is probably due to the action of the magma on the already formed crystals. Zinnwaldite, which is distinguished from lepidolite by the position of the optic axial plane, has not been before recorded from Ireland.

L. J. S.

**The so-called Schneebergite.** By ARTHUR S. EAKLE and WILHELM MUTHMANN (*Zeit. Kryst. Min.*, 1895, 24, 583—586).—Brezina gave this name to a mineral occurring as small, honey-yellow, regular octahedra at Schneeberg, Tyrol, stating that it consists essentially of antimony, calcium and a little iron (compare *Abstr.*, 1882, 150); it has, therefore, been considered to be near, or to be identical with, atopite. From the analysis made by the authors, it is, however, seen to be really a calcium iron garnet, neither antimony, bismuth nor copper having been detected.

$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	Total.	Sp. gr.
35.45	32.22	32.58	100.25	3.848

The material is rendered impure by inclosing, or being otherwise associated with, magnetite, blende, copper pyrites, quartz, calcite, and brannerite; the mineral having been derived from the last two. The occurrence of a topazolite without any alumina and as octahedra is of interest.

L. J. S.

**Delessite from Cantyre.** By M. FORSTER HEDDLE and J. STUART THOMSON (*Min. Mag.*, 1895, 11, 28—29).—A dark green delessite occurring as veins in the dolerite of Knockscalbert quarry, gave, on analysis

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.	Total.
34.69	5.48	10.82	18.71	2.49	12.21	15.19	99.59

7.29 per cent. of water was given off at 100°. Sp. gr. 2.608. Delessite is of much rarer occurrence in Scotland than saponite.

L. J. S.

**Crossite, a New Soda Amphibole.** By CHARLES PALACHE (*Bull. Geol. Dep. Univ. Calif.*, 1894, 1, 181—191).—This blue amphibole occurs as small prisms embedded in the white albite of the crystalline schists near Berkeley, California. The optical characters resemble those of riebeckite, the extinction angle of 13° being, however, greater; the pleochroism is very strong, varying from dark blue to yellowish. Sp. gr. 3.16. Analysis gave

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
55.02	4.75	10.91	9.45	trace	9.30	2.38	7.62	0.27	99.70

The composition is thus between that of riebeckite and that of glaucophane. The optical characters closely resemble those of a mineral from Colorado, described by Whitman Cross (*Amer. J. Sci.*, 1890, [3], 39, 359).

L. J. S.

**Urbanite, a New Pyroxene.** By S. A. HJALMAR SJÖGREN (*Geol. För. Förh.*, 1892, 14, 251—253; and *Bull. Geol. Inst. Upsala*, 1894, 2, 77—87, 106—108).—This mineral, which occurs as veins in hæmatite at the Långban mines, Sweden, was first examined by Breithaupt in 1865, it being then considered to be identical with the schefferite from the same locality. In drusy cavities, brilliant, brownish-black or black, monosymmetric crystals have been found; these have an octahedral habit, and their morphological and optical constants approach those of acmite rather than those of schefferite. Sp. gr. 3.52. The analysis I corresponds to the metasilicate formula (Ca,Mg)O,SiO<sub>2</sub> + Na<sub>2</sub>O,Fe<sub>2</sub>O<sub>3</sub>,4SiO<sub>2</sub>, the first part representing diopside, and the second part acmite. The high percentage of ferric oxide and of alkalis further distinguishes the mineral from schefferite.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
I. Långban,	51.61	—	0.74	27.24	0.54	1.73	4.90	2.75
II. Glakärn,	49.21	0.06	1.27	25.35	0.50	6.71	5.68	1.39

	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F.	Loss on ignition (probably water).	Total.
I.	0.36	10.59	—	—	0.90	101.36
II.	0.40	8.95	1.05	0.20	—	100.69

Igelström's "lindesite" from the Glakärn mine, Örebro (this vol., ii, 76), has been re-analysed by Mauzelius, giving the results under II, from which a similar formula to the above is deduced, namely, (Ca,Mn)O,SiO<sub>2</sub> + Na<sub>2</sub>O,Fe<sub>2</sub>O<sub>3</sub>,4SiO<sub>2</sub>, this representing, as regards composition, a rhodonite with an acmite molecule. The mineral occurs at this locality as embedded grains in manganese ores, and agrees in its physical characters with the urbanite of Långban. Sp. gr. 3.53.

L. J. S.

**Analyses of Nickel-silicate Ores.** By HEINRICH VON FOULLON (*Zeit. Kryst. Min.*, 1895, **24**, 643—644; from *Jahrb. k. k. geol. Reichsanst.*, 1892, **42**, 223—310).—Nickel silicates of very variable composition occur in veins in decomposed olivine rocks, the origin of the nickel being traced to the olivine, which mineral, in the harzburgite of Riddle, Oregon, contains 0.32 per cent. NiO, while the bronzite of the same rock contains scarcely a trace. The nickel ores of Revda in the Urals (I), Riddle (II), and New Caledonia (III) consist of light-green, optically uniaxial flakes, apparently hexagonal in outline; they seem to be talc-like minerals, with Ni in place of Mg, which approach garnierite. The ores from near Frankenstein, Silesia, were separated by washing into (IV) a yellowish-green material consisting of optically biaxial flakes, and (V) an apple-green material consisting of optically uniaxial flakes; both these were decomposed by hot hydrochloric acid, and, on heating, became tombac-brown in colour, and showed an increase in the optic axial angle; they appear to be related to the chlorites. VI and VII are also from near Frankenstein.

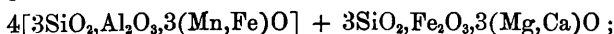
	I.	II.	III.	IV.	V.	VI.	VII.
SiO <sub>2</sub> .....	54.15	48.82	34.60	38.42	40.05	44.74	51.88
Al <sub>2</sub> O <sub>3</sub> .....	0.23	—	0.69	9.76	4.52	0.00	3.94
Fe <sub>2</sub> O <sub>3</sub> .....	0.27	0.06	0.52	5.68	2.20	1.29	2.33
FeO .....	—	—	—	0.59	0.53	—	1.19
NiO .....	27.61	19.04	46.87	8.88	21.17	27.02	2.97
MgO .....	6.82	18.49	5.35	20.22	18.23	15.38	22.76
CaO .....	—	—	—	—	trace	—	10.57
H <sub>2</sub> O at 100° .....	3.65	9.26	2.52	16.68	14.06	10.29	{ 1.16
H <sub>2</sub> O on ignition ..	4.09	3.03	7.68				{ 2.69
Total .....	96.82	98.70	98.23	100.23	100.76	98.72	99.49

L. J. S.

**Garnet Hornfels from Co. Dublin.** By WILLIAM J. SOLLAS (*Sci. Proc. Roy. Dublin Soc.*, 1891, N.S., **7**, 48—54).—This rock occurs in schists near the granite at Carrickmines; the bulk analysis is given under I, there being also traces of TiO<sub>2</sub> and K<sub>2</sub>O; sp. gr. 2.925. It contains the minerals ilmenite, garnet (II, sp. gr. 4.16), green manganese-mica (III, sp. gr. 2.795—3.01), and muscovite in a mosaic of quartz and felspar.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.
I.	48.61	21.61	10.92	2.26	12.09	0.51	0.05	3.02	2.10
II.	37.63	16.43	7.85	14.59	18.55	3.49	2.10	—	—
III.	35.62	16.21	22.01	—	16.55	—	—	2.87	6.52

The garnet is represented by



the iron of the mica exists mostly in the ferrous state. The rock is supposed to have originated by the contact-metamorphism of a manganese-bearing slate.

L. J. S.

**The Leinster Granites.** By WILLIAM J. SOLLAS (*Jahrb. f. Min.*, 1895, ii, 80—85; from *Trans. Roy. Irish Acad.*, 1891, 29, 427—514).—As is well known, the granite of this area is a two-mica granite; only at two points does a granitite (that is, biotite-granite) occur. The rocks are divided into two types—soda granites, and potash granites. The soda granite of Aughrim gave analysis I, and the proportions of the constituents were determined as, sphene and epidote, 0.546; primary mica, 7.328; zonal feldspar, 51.143; microcline, 9.193; quartz, 31.790 per cent.; sp. gr. 2.68. A porphyritic dyke from this granite gave the results under II. The minerals of the granite were separated by means of the author's graduated column of a heavy solution (*Nature*, 1891, 43, 404; 1893, 49, 211), and each described in detail. The dark mica, haughtonite, from Aughrim, gave the results under III, and for it the formula  $\text{Si}_{12}\text{R}'''\text{R}''\text{R}'_{13}\text{O}_{48}$  is derived. The soda lime feldspars are represented by all the members of the series, and the amounts of the alkalis in several of different sp. gr. are given; IV gives the analysis of albite, of sp. gr. 2.628, from Three Rock Mountain. Microcline from the last locality, of sp. gr. 2.57, gave 12.15 per cent. of  $\text{K}_2\text{O}$  and 3.69 of  $\text{Na}_2\text{O}$ .

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .
I.	70.69	15.20	3.76	—	3.31	0.45	2.31	4.69	0.56
II.	71.78	15.86	4.19	—	3.16	0.50	1.13	4.10	1.17
III.	33.95	17.13	2.44	21.18	2.03	6.60	7.12	2.83	3.70
IV.	67.17	20.50	0.22	—	1.61	trace	10.16	0.65	0.31
			$\text{TiO}_2$ .	$\text{P}_2\text{O}_5$ .	F.				
III. (contd.)			3.81	0.68	trace				

The author develops Tschermak's hypothesis of the composition of the micas, giving as a nucleus to his structural formula a "silica ring" consisting of six silicon and six oxygen atoms alternating; the two remaining valencies of each silicon being joined to such groups as  $\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O} > \text{R}''' \cdot \text{O} \cdot \text{R}'$ ,  $\begin{smallmatrix} \text{O} \cdot \text{R}'' \\ \diagdown \end{smallmatrix} > \text{O}$ ,  $\begin{smallmatrix} \text{O} \cdot \text{R}'' \cdot \text{O} \cdot \text{R}' \\ \diagdown \end{smallmatrix}$ , &c. Thus a biotite having, according to Tschermak, the composition  $2(\text{H}_2\text{KAl}_3\text{Si}_3\text{O}_{12}) + \text{Mg}_6\text{Si}_3\text{O}_{12}$ , is represented by a silica ring with four of the first of the above groups and two of the second.

L. J. S.

**Water of the Sea of Marmora.** By KONRAD NATTERER (*Monatsh.*, 1895, 16, 405—581; compare *Abstr.*, 1893, ii, 216: 1894, ii, 102).—The author gives a detailed account of the investigations made during the expedition of the ship "Taurus" in the sea of Marmora in May, 1894. The results obtained in the exact determination of the physical and chemical properties and condition of the water at 44 different stations and at various depths are fully set out, and are such as, on the whole, might be expected from the position of a deep sea connected at one end with the Ægean Sea by the Dardanelles, and at the other with the Black Sea by the relatively shallow Bosphorus. A full description of the analytical methods and of the apparatus employed is given, and this is supplemented by numerous tables, charts, and diagrams.

G. T. M.

## Physiological Chemistry.

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**Is Argon contained in Vegetable or Animal Substances ?** By GEORGE W. MACDONALD and ALEXANDER M. KELLAS (*Proc. Roy. Soc.*, 1895, **57**, 490—492).—The authors have examined the gases obtained by nitrogen estimations, performed by Dumas' method, in order to determine the absence or presence of argon. They conclude that there is no appreciable quantity of argon in either vegetable or animal substances, or at least that the argon is not liberated with the nitrogen in Dumas' method. E. C. R.

**Pepsin.** By AUGUSTIN WRÓBLEWSKI (*Zeit. physiol. Chem.*, 1895, **21**, 1—18).—The pepsins obtained from the stomachs of children, dogs, and pigs behave differently in the presence of different acids, and in this respect, moreover, they are different from one another. Twelve acids in all were used in the experiments, and their beneficial effect on peptic activity is not proportional to their strength. Using equivalent quantities of acid, oxalic was found to be that most favourable to digestion, and hydrochloric acid comes next. Certain alkaloids also are not without influence; for instance, caffeine is the one which acts most favourably, and veratrine that which acts most injuriously on gastric digestion. The casein of cow's milk is recommended as a good substance for testing the activity of pepsin mixtures.

W. D. H.

**Kühn's Method of Artificial Digestion of Nitrogenous Food Constituents by Pepsin Solution.** By A. KÖHLER, F. BARNSTEIN, and W. ZIELSTORFF (*Landw. Versuchs-Stat.*, 1895, **46**, 193—200).—Kühn's artificial digestion method (*Abstr.*, 1894, ii, 390) may be simplified by adding the hydrochloric acid (11 per cent.) in two portions, 15 c.c. at the commencement of the experiment, and 25 c.c. after 24 hours, instead of in smaller quantities at short intervals. In most cases it is unnecessary to extract the fat before submitting the food to the action of the pepsin solution. N. H. J. M.

**Influence of Fat and of Starch on Metabolism.** By A. WICKE and HUGO WEISKE (*Zeit. physiol. Chem.*, 1895, **21**, 42—67).—The point specially investigated is the influence of non-nitrogenous food on nitrogenous metabolism. The experiments were made on two sheep, the food, fæces, and urine being analysed and compared in the usual way. The main results were as follows:—Administration of starch lessens the digestion and absorption of fat, and especially of proteids and cellulose. Administration of fat does not have this effect. In both cases, the amount of fæces (dried) was increased; after starch, the water in the fæces is increased; after fat, it is not.

W. D. H.

**Influence of the Thyroid Gland on Metabolism.** By ERNST ROOS (*Zeit. physiol. Chem.*, 1895, **21**, 19—41).—The history of the subject, so far as it relates to the use of thyroid extract in the relief



of myxœdema, is first given. Observations on men showed a marked increase of excretion of phosphoric acid while under treatment; the greater number of the experiments related, however, were made on dogs; the thyroid had been previously removed, and then the gland was administered as food to them. The urine and fæces were analysed. Some control experiments were made on healthy dogs. In the latter there is increase of nitrogen (more than can be explained by the nitrogen in the gland given), of sodium chloride, and phosphoric acid excreted. The rise in sodium chloride does not last so long as the others.

In dogs without a thyroid, the increased excretion of nitrogen and chlorine is more marked than in healthy animals, whilst the rise in the excretion of phosphoric acid is not so marked. There is also a diuretic action.

Some attempts to separate and identify the active substance in the thyroid were made. This part of the research is incomplete. So far as it goes, it shows that the substance is pretty stable; it is not an enzyme, and is probably proteid-like in nature. W. D. H.

**Acid Fodder and its Effects on the Organism.** By HUGO WEISKE (*Zeit. physiol. Chem.*, 1895, 20, 595—605).—The experiments were made on rabbits, and the effects to which particular attention is drawn are those in the skeleton. Oats have, in contrast with hay, mineral constituents with an acid reaction. Animals fed on oats and other grains alone, suffer and die. At first the weight increases, but soon an acid reaction of the urine sets in, the body loses weight, and marked effects on bones and teeth are evident. In young animals, the poverty of oats in calcium also produces an effect. These facts are illustrated by experiments on rabbits of the same litter and different diets. Some were fed normally, others on oats *plus* either calcium sulphate or phosphate. The animals, 47 days later, were killed. The following table gives the main analytical results:—

Diet.	Oats + $\text{CaSO}_4$ .	Oats + $\text{Ca}_3(\text{PO}_4)_2$ .	Normal.
Bone, dried and fat free	53·032 gram	56·862 gram	59·417 gram
Organic constituents. . .	19·706 "	20·908 "	22·916 "
Mineral " . . .	33·326 "	35·954 "	36·501 "
CaO . . . . .	17·144 "	18·406 "	18·711 "
MgO . . . . .	0·372 "	0·409 "	0·463 "
CO <sub>2</sub> . . . . .	1·541 "	1·746 "	1·785 "
P <sub>2</sub> O <sub>5</sub> . . . . .	13·242 "	14·108 "	14·462 "
Remainder . . . . .	1·028 "	1·285 "	1·080 "

The total weight of the bones (dried) is less than in normal animals; the percentage of fat in both bone and teeth is considerably over the normal, but the water is diminished. In animals to which calcium salts are not given, the fall in mineral salts is even more marked; and in periods longer than in the experiment quoted this is also the case. W. D. H.

**Distribution of Assimilated Iron Compounds, other than Hæmoglobin and Hæmatins, in Animal and Vegetable Cells.**

By A. B. MACALLUM (*Proc. Roy. Soc.*, 1895, **57**, 261—262; see also *Proc. Roy. Soc.*, **50**, 277).—The reagent which proved to be of the greatest service for liberating the iron of assimilated compounds was freshly prepared ammonium hydrosulphide, made from a solution of ammonia of 0.96 sp. gr., and applied, mixed with glycerol, to the isolated cells in the way already described. Sulphuric, hydrochloric, and nitric acids dissolved in 95 per cent. alcohol liberate the iron of assimilated compounds, but the results obtained with these acids were controlled by experiments with the sulphide reagent when this was possible. The iron liberated is readily demonstrated as ferrous sulphide or as Prussian blue.

Iron, firmly combined, is a constant constituent of animal and vegetable chromatin. Another compound, less rich in iron, is found in nucleoli. The chromophilous substance in ferment-forming cells contains iron, and the cytoplasm of Protozoan organisms, which also probably secretes ferments, yields evidence of the presence of a firmly combined iron compound. A compound of iron is present in the chromophilous substance of the cytoplasm of fungi. Of the non-nucleated organisms, Bacteria, owing to their minuteness, have, with one exception, given little evidence of the presence of an organic iron compound; but in the Cyanophycæ the chromophilous portions of the central substance contain iron, and iron is also present in the peripheral granules formed of the so-called cyanophycin.

E. C. R.

**Nucleo-proteïds.** By WILLIAM D. HALLIBURTON (*J. Physiol.*, 1895, **18**, 306—318).—The proteïd formerly termed  $\beta$ -cell-globulin by the author is really a nucleo-proteïd. This is true whether it is obtained from the stromata of the red blood corpuscles or from lymphoid structures like the thymus. On gastric digestion, it yields an insoluble residue of nucleïn, and its physiological action is similar to that of other nucleo-proteïds. Schmidt's fibrin ferment comes under the same category. It does not produce intravascular clotting, because the method of preparation, involving, as it does, the use of alcohol, leads to the formation of extremely dilute solutions, which, like all dilute solutions of nucleo-proteïd, causes a "negative phase," that is, a hindering influence on the coagulation of intravascular blood. Details of experiments are given, which support Pekelharing's contention that fibrin ferment is a calcium compound of nucleo-proteïd, and that the action of nucleo-proteïd in not promoting the coagulation of extravascular (salted) plasma is due to the inhibitory influence of the magnesium sulphate or other salt employed in the obtaining of the plasma. A number of phosphorus estimations in these and other varieties of nucleo-proteïd are also given, the amount of phosphorus in that of red marrow being especially high.

W. D. H.

**Chemical Phenomena of Ossification.** By P. CAMILLE CHABRIÉ (*Compt. rend.*, 1895, **120**, 1226—1228).—The author has previously found (*Abstr.*, 1894, ii, 325) that the conversion of the fundamental cartilagenous matter into the fundamental osseous matter is the

result of a simultaneous oxidation and the substitution of the amido-group for the hydroxyl group, the change being brought about by the influence of ammonia or ammonium salts in an alkaline medium, but not in presence of lactic acid. The same change seems to be brought about in the organism by urea in consequence of its ready convertibility into ammonium salts. Ammonium carbonate destroys the blood corpuscles, with liberation of lecithin, which acts as a feeble base and combines with carbonic acid. If lecithin, emulsified in water, is added to a mixture of sodium hydrogen phosphate and sodium hydrogen carbonate, to which some calcium chloride has been added, a precipitate of calcium carbonate and phosphate is formed, owing to the combination of the lecithin with the carbonic acid that would otherwise keep them in solution. It would seem, therefore, that the lecithin set free by the destruction of blood corpuscles is one of the main causes of calcification. In presence of lactic acid, as in cases of osteomalagia, this precipitation of calcium salts could not take place, and the action of the acid on the lecithin would liberate fatty acids, which are always present in such cases. The presence of relatively high proportions of magnesium salts under the same conditions arises from the fact that the solubilities of calcium and magnesium salts of fatty acids are practically the same in dilute solutions of lactic acid, whereas in normal ossification the conditions are not such as favour the precipitation of magnesium salts.

C. H. B.

**Composition of the Bones, Teeth, &c., of Wild and Tame Rabbits.** By HUGO WEISKE (*Landw. Versuchs-Stat.*, 1895, 46, 233—238; compare Abstr., 1894, ii, 287).—A comparison of wild and tame rabbits showed that whilst the former had the larger proportion of flesh and the smaller proportion of bones, the amount of digestive organs was almost identical in both. The skeleton of the wild rabbits contained on the average, 29·2 per cent. of water and 8·5 per cent. of fat, that of the tame rabbits 37·9 per cent. water and 8·6 fat. The amount of organic matter, total ash, and ash constituents was determined in the teeth, in the long tubular bones, and in the other bones. Variations occur in the composition of the bones of both tame and wild rabbits. The bones, especially the long tubular bones of the wild rabbits, contain more total ash than those of the tame rabbits, the difference being most marked in the case of lime and carbonic anhydride. The composition of the teeth is much more constant, but the teeth of wild rabbits seem to contain rather less mineral constituents than those of tame rabbits. It is possible that the age (which was not known) of the wild rabbits had something to do with the amount of calcium carbonate (compare L. Graffenberger, Abstr., 1891, 1275).

N. H. J. M.

**Paranuclein in the Animal Organism.** By W. SANDMEYER (*Zeit. physiol. Chem.*, 1895, 21, 87—88).—Paranuclein was prepared from casein; it contained 0·156 per cent. of phosphorus, which was almost exclusively in organic union. This was given to a dog; the urine in the 24 hours contained from 0·33 to 0·37 grams of phosphoric anhydride, but after the administration of paranuclein it rose to 1·34

on one, and 1·84 on another, occasion. This shows that the phosphorus in organic form in casein is absorbed from the alimentary canal, and fits in with recent researches, which have shown that the phosphorised compound in casein is dissolved in the stomach partly, and by the pancreatic juice almost entirely.

W. D. H.

**Uric Acid Excretion.** By KARL DAPPER (*Chem. Centr.*, 1895, i, 163; from *Therap. Monatsh.*, 8, 522).—The absolute amount of uric acid excreted varies greatly in the same individual and in different people. Its relationship to the total nitrogen varies with the different percentages of proteid in the food from 23·2 to 122·4. There is, moreover, no relationship between uric acid and body weight; for 100 kilos. of the latter, the former varies from 0·528 to 1·829 grams. E. Pfeiffer's figures are criticised.

W. D. H.

**Acidity of Urine.** By VICTOR LIEBLEIN (*Zeit. physiol. Chem.*, 1895, 21, 97—108).—Polemical (compare this vol. ii, 279).

W. D. H.

**Levulose in Diabetes.** By W. HALE WHITE (*Chem. Centr.*, 1895, i, 167; from *Zeit. Klin. Med.*, 26, 332).—In three cases of diabetes mellitus, the administration of levulose was found to increase the amount of sugar in the urine, and some of this sugar was levulose. This is contrary to what Minkowski found. The amount of urine was also increased. Allowing for the amount of levulose in the urine, the rest of the sugar was lessened, and the patients gained weight. Inulin also increases the body-weight, but increases the output of sugar, and this increase is not wholly explicable by the increased intake of carbohydrate.

W. D. H.

**Levulose in Diabetes.** By KARL GRUBE (*Chem. Centr.*, 1895, i, 167—168; from *Zeit. Klin. Med.*, 26, 340—345).—In slight cases of diabetes, levulose can be given in large quantities without harm. The organism in this disease appears able to use this sugar better than any other.

W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Vegetable Assimilation and Respiration: The Carbonic Anhydride Exchanges of Plants.** By F. FROST BLACKMAN (*Proc. Roy. Soc.*, 1895, **57**, 162—164, and 165—168).—The author describes an apparatus in which the evolution of carbonic anhydride by a single germinating seed, or by a small area of a foliage leaf, can be accurately estimated from hour to hour without a break, whilst for the same area of leaf the more active absorption of carbonic anhydride in assimilation can be easily determined for such short periods as 15 minutes, and that at the same time separately for the two surfaces of one and the same leaf area. The estimation of the carbonic anhydride is made by the well-known method of absorption by baryta.

solution and titration with hydrochloric acid. The apparatus is arranged so that this estimation can be carried out in the apparatus itself, and so that a current of air, either free from carbonic anhydride, or containing a definite quantity of the same, can be supplied continuously at atmospheric pressure to either surface of the leaf.

To determine the path of gaseous exchange between aerial leaves and the atmosphere, shallow capsules 10 sq. cm. in area are affixed to a leaf on opposite sides of the same area by means of soft wax, and then two continuous currents of air are kept up over the two surfaces, and the carbonic anhydride produced or taken in, during a given time, by each of them is determined. The results obtained show that under normal conditions practically the sole pathway for carbonic anhydride into, or out of, the leaf is by the stomata. Since oxygen diffuses more readily than carbonic anhydride through fine openings, the same probably holds for oxygen, and the whole of the gas exchange. Under abnormal conditions, when the stomata or inter-cellular spaces are blocked, and the surrounding tension of carbonic anhydride is great enough, passage of carbonic anhydride by osmosis through the cuticle may take place. Such closure of stomata as is held to take place in darkness does not prevent the distribution of gas exchange closely agreeing with that of the stomata. The exhalation of carbonic anhydride in bright light by a leafy shoot in Garreau's well-known experiment, is not the expression of any physiological truth for the leaf, but only due to the imperfections of the conditions, to the presence of immature parts, or of tissues not sufficiently green, or not fully illuminated. Mature isolated green leaves, fully illuminated, assimilate the whole of their respiratory carbonic anhydride, and allow none to escape from them.

E. C. R.

**Germination of Seeds.** By TH. SCHLOESING, JUN. (*Compt. rend.*, 1895, 120, 1278—1280.)—Wheat and white lupins were allowed to germinate in moist sand in a confined atmosphere, the volume and composition of which were accurately known. Oxygen was introduced from time to time, in order to maintain the proportion at about 21 in 100, but no carbonic anhydride was introduced. When the plants had attained considerable size, the gas in the vessels was withdrawn, measured, and analysed. The results show that during the germination of wheat and lupins, none of the nitrogen originally present in the seed is liberated in the gaseous form.

C. H. B.

**Utilisation of Elementary Nitrogen by Mustard.** By THEODOR PFEIFFER and E. FRANKE (*Landw. Versuchs-Stat.*, 1895, 46, 117—151).—After discussing and pointing out the inconsistencies in Liebscher's results (*Abstr.*, 1894, ii, 201), the authors describe their own experiments made on similar lines. The plan followed was to grow, first peas, then mustard, in the same soil, under various conditions. There were three series, each of six pots. (I) sterilised; (II) sterilised, and then inoculated; and (III) not sterilised. The soil contained 0.0392 per cent. of nitrogen (= 10.584 grams per pot containing 27 kilos. of soil). Half of the pots of each series received 1.2 grams of nitric nitrogen for mustard; the necessary minerals were added.

As regards the pea experiment, there was no great difference in the amounts of dry produce, the average amount being 54.95 grams, containing an average amount of 1.30 grams of nitrogen. No satisfactory balance of total nitrogen could be obtained, owing to the difficulty of sampling.

In the mustard experiments, as in the case of peas, it was for the same reason impossible to obtain a balance of total nitrogen, but the results, taking the produce alone, were very regular and consistent, and the figures obtained from the three pots of each experiment agreed very nearly. The following are the average results.

Experiments.	Dry produce.	N. in produce.
1, 2, 3 without nitrate, sterilised .....	27.6	0.4323
7, 8, 9 " " " and inoculated....	30.1	0.4276
13, 14, 15 " " not sterilised .....	14.8	0.1546
4, 5, 6 with nitrate sterilised .....	71.2	1.4688
10, 11, 12 " " " and inoculated	68.5	1.5169
16, 17, 18 " " not sterilised .....	63.4	1.1938

The effect of nitrate is thus very marked.

The higher results obtained in the pots which had been sterilised as compared with those of the pots which were not sterilised are, no doubt, due to the action of the heated steam by which the soil constituents were rendered more soluble. In comparing the effect of nitrate on the amount of nitrogen in the produce, this inequality may be eliminated by deducting the total nitrogen of the sets which had no nitrate, from that of the corresponding sets which had nitrate; the resulting figures then show the increase due to nitrate: sterilised, 1.0365; sterilised and inoculated, 1.0893 (?1.0393); not sterilised, 1.0392 gram. The results are practically identical, and show that soil bacteria were without effect on the yield of nitrogen. The nitric nitrogen applied was 1.2 gram; the average amount of nitrogen in the produce due to nitrate added was 1.055 gram; this excess is therefore fully accounted for without assuming fixation to have taken place. The results point to the conclusion that mustard cannot utilise elementary nitrogen.

It is hoped in subsequent experiments, by means of more perfect sampling, to obtain a satisfactory balance of total nitrogen, although, owing to the fact that nitrogen fixation may take place in soil, such a nitrogen balance is not essential. N. H. J. M.

**Influence of the Root-nodules of *Alnus Glutinosa* on the Fixation of Nitrogen.** By LORENZ HILTNER (*Landw. Versuchs-Stat.*, 1895, 46, 153—161).—The results of the author's experiments with the common alder point to the following conclusions. The plants do not develop in absence of combined nitrogen, unless provided with root nodules, whilst with root nodules the plants utilise free nitrogen similarly to the *Papilionaceæ*. In presence of combined nitrogen in the soil, the production of nodules is hindered, or may be

stopped altogether; nodules are, however, formed in increased amount as the soil becomes poorer in available nitrogen. The organism which produces nodules in the alder roots acts as a parasite until the nodule is fully developed, after which the plant benefits.

Unlike the pea nodules, the alder nodules are effective in water cultures; addition of nitrate to such cultures hinders or stops the development of the nodules.

R. Dinger (*Landbouwkund. Tijdschr.*, 1895, **3**, 167—192) also concluded that the alder assimilates free nitrogen when provided with root nodules.

N. H. J. M.

**Composition of the Root Nodules of the Alder.** By ADOLF MAYER (*Landbouwkund. Tijdschr.*, 1895, **3**, 319—320).—The following numbers show the percentage composition of (1) the nodules, (2) the roots of the alder in the dry state.

	Crude protein.	Protein.	Nitrogen free* extract.	Crude fibre.	Ash.
(1) ....	9.8	(8.3)	64.6	17.4	8.2
(2) ....	5.7	(5.4)	60.5	31.8	2.0

Troschke found the following percentage amounts in the dry matter of (1) the nodules, (2) the roots of blue lupins.

	Crude protein.	Protein.	Nitrogen free extract.	Crude fibre.	Crude fat.	Crude ash.
(1) ....	45.3	31.6	32.5	9.4	5.3	7.5
(2) ....	7.1	5.2	34.6	52.9	1.3	4.1

The crude ash of the lupin nodules and roots contained  $K_2O$  (1), 16.6; (2), 12.8;  $P_2O_5$  (1), 16.19; (2), 8.84 per cent. (*Wochenschr. d. Pommersch. ök. Ges.*, 1884, No. 19, and Abstr., 1885, 420).

N. H. J. M.

**Cane Sugar in Plants.** By ERNST SCHULZE and S. FRANKFURT (*Zeit. physiol. Chem.*, 1895, **20**, 511—555; **21**, 108).—The chemical part of this paper has been previously published (Abstr., 1894, i, 154). With regard to the physiological uses of cane sugar, the general conclusion is drawn that it is not only a most valuable reserve material in plant life, but that it also plays a very important rôle as a circulating condition (*Wanderungsform*) of starch. It is almost always accompanied by other soluble forms of carbohydrate, but these are not regarded as having the same function as cane sugar, as the nature and amount of these other carbohydrates vary considerably in different vegetables. They are possibly reserve stuffs, and probably are changed during the life of the plant into cane sugar.

In the second paper, the authors make a correction. They previously said that from cane sugar and three other carbohydrates, invertin was able to form glucose. This was written previous to Fischer's work on invertin (this vol., i, 161, 141; ii, 322). Instead of invertin, it would be now better to say a preparation of enzymes from yeast, for such preparations probably contain several enzymes.

W. D. H.

\* Including a little fat.



**Origin of Unsaturated Compounds in Plants.** By CHARLES F. CROSS, EDWARD J. BEVAN, and CLAUD SMITH (*Ber.*, 1895, **28**, 1940—1945).—See this vol., i, 640.

**Chemical Investigation in Plant Pathology.** By JULIUS STOKLASA (*Zeit. Physiol. Chem.*, 1895, **21**, 79—86).—The chemical processes investigated are those occurring in the sugar beet when attacked by the parasitic nematode, *Heterodera Schachtii*, the production of saccharose being lessened; in damp soil, the injurious effect of the parasite is doubled. The fundamental change appears to be in the living molecules, leading to a partial oxidation of the circulating proteid of the plant protoplasm; the proteid in the leaves sinks, whilst the asparagine (or glutamine) is increased. W. D. H.

**The Tobacco Plant.** By J. BEHRENS (*Landw. Versuchs-Stat.*, 1895, **46**, 164—192).—In the process of drying tobacco leaves by keeping them in heaps, the whole becomes heated in the same manner as malt, &c. The so-called "scalding" of the leaves is not caused through the killing of the leaves by heating, but through the poisonous effect of the accumulation of carbonic anhydride, and perhaps, in part, by the action of micro-organisms. The only advantage of the process over the ordinary drying process seems to be the saving of time. In both processes, the leaves contain the same percentage of total nitrogen, but in the heated leaves, a much larger proportion of the nitrogen is in the form of proteids. This is connected with the conversion of the starch into sugar, observed in leaves dried in masses, it being supposed that the sugar reacts with the products of decomposition of the proteids to re-form protein.

An examination of the moulds and bacteria of tobacco leaves, and of snuff, was made. The manufacture of snuff is discussed, and suggestions made for improving the quality of tobacco.

N. H. J. M.

**Behaviour of Phosphoric acid, Soluble in Water, towards the Absorbent Constituents of Soil.** By MAX GERLACH (*Landw. Versuchs-Stat.*, 1895, **46**, 201—219).—For estimating the available phosphoric acid, extraction with 1 per cent. citric acid solution was found very suitable for the great majority of soils (compare Dyer, *Trans.*, 1894, 115). It frequently occurred, however, that soils which were not benefited by applying superphosphate yielded comparatively small quantities of phosphoric acid by this method; this was especially the case with light, sandy soils. Only one case was observed in which a soil yielding a good deal of phosphoric acid when treated with citric acid, gave a heavier crop when manured with superphosphate. Attempts to explain these unexpected results have not yet been entirely successful.

As regards the effect of soil constituents (compare A. Thomson, *Verhalten d. Sandbodens gegen Superphosphat*) in retaining soluble phosphates, the results of experiments now recorded, show that clay, peat, and sand which have been extracted with hydrochloric acid have no power of absorbing free phosphoric acid, sodium phosphate, or superphosphate; calcium and magnesium carbonates both absorb

phosphoric acid applied in the three forms, whilst alumina and ferric hydroxide do so very completely. Sodium phosphate is the least readily retained. The phosphoric acid so absorbed by the two carbonates is comparatively readily soluble, and is completely extracted by water containing carbonic anhydride. Phosphoric acid absorbed by ferric hydroxide and alumina becomes insoluble in water, even in presence of carbonic anhydride, but is more or less completely dissolved by the prolonged action of dilute organic acids.

Experiments were next made to ascertain in what form the phosphoric acid is absorbed. When a solution of hydrogen calcium phosphate comes into contact with calcium carbonate, di- and tricalcium phosphates are produced, according to the amount of calcium carbonate present (compare Stoklasa, *Abstr.*, 1893, ii, 549). When ferric hydroxide and alumina are the absorbents, not only the phosphoric acid, but the lime is also precipitated; dicalcium phosphate and an iron (or aluminium) phosphate are formed. An air-dried mixture of ferric hydroxide, ferric phosphate, and dicalcium phosphate, when mixed with sand and extracted with carbonic acid water, gave up the whole of the lime, but practically no phosphoric acid.

Four lots of soil (each 100 grams) were treated with 1 litre of 1 per cent. acetic acid. When filtered immediately, 0.0145 gram of  $P_2O_5$  was dissolved, whilst when the action was continued for 3 hours, 24 hours, and 14 days respectively, 0.0103, 0.0079, and 0.0024 gram of  $P_2O_5$  were dissolved, the effect of the acetic acid being to dissolve at once the more readily soluble phosphates, which were then gradually fixed by the alumina or ferric hydroxide in the soil (compare Wagner, *Journ. f. Landw.*, 1871, 100). An action similar to that described might be imagined to take place in a soil manured with superphosphate, the solvent in this case being water and carbonic anhydride (compare Georgieris, *Chem. Zeit.*, 1891, 1626). A loamy soil, containing CaO 0.86,  $P_2O_5$  0.086, per cent. (insoluble in citric acid) was saturated with a solution of superphosphate; when extracted with water containing carbonic anhydride, a large quantity of lime was dissolved, but no phosphoric acid. Under natural conditions, the process would, no doubt, be much slower.

N. H. J. M.

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### Analytical Chemistry.

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**Valve Pipette.** By OSCAR BOCK (*Zeit. anal. Chem.*, 1895, **34**, 432—433).—The pipette body is of the ordinary form, but instead of the narrow upper tube it is fitted with a rod, sliding in a detached guide tube, and ground at its lower end to a conical valve; this fits into a seat at the summit of the pipette body, and by its means the top of the pipette can be opened or closed. M. J. S.

**Potassium Hydrogen Iodate in Volumetric Analysis.** By C. MEINERKE (*Chem. Zeit.*, 1895, **19**, 2—7).—Potassium hydrogen iodate,

$\text{KHI}_2\text{O}_6$ , is recommended by the author for the standardising of various volumetric solutions, on account of its great purity and stability. Mixed with a large excess of potassium iodide and a sufficiency of hydrochloric or sulphuric acid, its molecule liberates 12 atoms of iodine, and the solution may then be used in all cases where volumetric iodine is wanted. Mixed with potassium iodide without acid, part of its iodine is set free, and may be removed by means of sodium thiosulphate. The resulting solution when acidified liberates a further amount of iodine, dependent on the quantity of acid added; the compound is therefore useful in acidimetry. The acid nature of the salt makes it also suitable for the standardising of alkaline reagents, best with phenolphthaleïn as indicator.

L. DE K.

**New Reactions of Hydrogen Peroxide.** By LUDWIG ILOSVA DE NAGY ILOSVA (*Ber.*, 1895, **28**, 2029—2031; compare this vol., ii, 239).—The application of aniline in acid solution mixed with potassium dichromate as a test for the presence of hydrogen peroxide, has been already described by A. Bach (*loc. cit.*); the author's experiments show that dimethylaniline, paramidobenzenesulphonic acid, ortho- and para-toluidine, tolylenediamine, xylydene, and naphthylamine may be advantageously employed, whilst diphenylamine and methyl-diphenylamine give no characteristic coloration.

Particulars of the reactions are collected in the following table.

Reagent.	Dilution.	Reaction.
Aniline.....	1 in 1,000,000	Pale violet after 3 minutes.
Dimethylaniline .....	1 in 1,000,000	Yellow after one minute.
„ .....	1 in 5,000,000	Yellow after 5 minutes.
Paramidobenzenesulphonic acid	1 in 1,000,000	Reddish-violet after 1 minute.
Orthotoluidine.....	1 in 1,000,000	After 6 minutes becomes yellow, then green.
Paratoluidine.....	1 in 1,000,000	Coppery-red after 5 minutes.
Tolylenediamine .....	1 in 1,000,000	Pale rose-red after 2 minutes.
Xylydene .....	1 in 1,000,000	Rose-red after 3—4 minutes; reddish violet after 5 minutes.
Naphthylamine.....	1 in 1,000,000	Becoming colourless after 3 minutes, is bluish-violet at the end of 10—12 minutes.

M. O. F.

**Gas Volumetric Estimation of Hydrochloric acid in the Contents of the Stomach.** By V. MIERCZYNSKI (*Chem. Centr.*, 1895, i, 131—132; from *Centr. innere Med.*, **15**, 1073—1077).—A measured quantity of gastric juice (5—20 c.c.) is evaporated to dryness in a porcelain crucible, with the addition of barium carbonate. The residue is ignited, and the ash extracted with boiling water. If this solution should turn red with phenolphthaleïn, air must be passed through until the free baryta has been neutralised. The liquid, which contains barium chloride, is precipitated by means of a small excess of

ammonium chromate, and the barium chromate well washed with hot, very dilute ammonia. It is then rinsed with warm, dilute hydrochloric acid (1—20) into the outer container of Wagner's nitrometer, and mixed with 10 c.c. of dilute sulphuric acid. It is then, in the usual way, brought into contact with 10 c.c. of solution of hydrogen peroxide, and the liberated oxygen is finally measured. One molecule of oxygen represents 1 mol. of hydrochloric acid. The results are correct.

L. DE K.

### Detection and Estimation of Chlorate in Bleaching Powder.

By C. REMIGIUS FRESSENIUS (*Zeit. anal. Chem.*, 1895, **34**, 434—436).—In Pattinson's experiment on the formation of chlorate in bleaching powder when kept (*Abstr.*, 1888, 552), the chlorate was estimated by a differential method, and the results presented anomalies. A direct estimation can be made by allowing the hypochlorite to react with lead acetate, when the following reactions occur:— $\text{Ca}(\text{ClO})_2 + \text{PbCl}_2 = \text{PbO}_2 + \text{CaCl}_2 + \text{Cl}_2$ , and  $2\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = \text{PbCl}_2 + \text{PbO}_2 + 4\text{HC}_2\text{H}_3\text{O}_2$ . Twenty grams of the bleaching powder is rubbed up with water, made up to a litre, and filtered. Fifty c.c. of the clear filtrate is mixed in a flask with excess of neutral lead acetate. When no more precipitate can be obtained on further addition of lead acetate, the mixture is allowed to remain in an un-closed flask until the odour of chlorine has completely disappeared, which will be the case after 8—10 hours, and is then filtered. For qualitative testing, the lead is removed by adding a small excess of dilute sulphuric acid and filtering; a little indigo is then added, and sulphurous acid solution drop by drop, when the chloric acid is reduced to substances which bleach the indigo. For quantitative estimation, the precipitate of lead peroxide and chloride is washed; the washings are concentrated and the solution mixed with a small excess of sodium carbonate. The soluble matters are washed out of the precipitate, and the filtrate after being evaporated almost to dryness, is distilled with concentrated hydrochloric acid into potassium iodide.

M. J. S.

**Estimation of Sulphur in Iron.** By MORITZ A. v. REIS (*Chem. Centr.*, 1895, i, 129—130; from *Stahl u. Eisen*, 1894, 963—966).—The author recommends the process by which the sulphur is evolved as hydrogen sulphide and then oxidised by means of hydrogen peroxide in ammoniacal solution. The following precautions should be observed:—The solvent should consist of hydrochloric acid (sp. gr. 1.19) diluted with an equal bulk of water, and the distillation should be stopped when the liquid becomes thick and begins to froth. Care must be taken to have pure hydrogen peroxide, hydrofluosilicic acid being especially objectionable. To expel the last traces of gas, a current of hydrogen, or even a slow current of air, may be employed, but carbonic anhydride is not to be recommended, as this seems to prevent full oxidation. As small quantities of sulphuric acid are oxidised to persulphuric acid, which is not precipitated by baryta, this and the excess of hydrogen peroxide must be completely destroyed by boiling with hydrochloric acid and adding a slight excess of potassium permanganate, which is then in turn cautiously removed

by adding a little oxalic acid solution. If the amount of sulphate is very small, the separation of the precipitate will be promoted by adding an accurately measured quantity of sulphuric acid of known strength. The washed and ignited barium sulphate does not, as a rule, require purification.

L. DE K.

**Estimation of Sulphur in Iron.** By LUCIEN L. DE KONINCK (*Chem. Zeit.*, 1895, **19**, 502).—The author believes that although air does not readily oxidise hydrogen sulphide, yet it quickly oxidises the ferrous chloride, which then in turn acts on the hydrogen sulphide, and so causes a loss by precipitating sulphur. He therefore advises dissolving a little tin in the hydrochloric acid previous to use, so as to prevent the oxidation of the iron solution. There is no danger of any tin sulphide being formed if the acid is only strong enough.

L. DE K.

**Estimation of the total Sulphur in Urine.** By PAUL MOHR (*Zeit. physiol. Chem.*, 1895, **20**, 556—561).—In estimating the total sulphur in urine, three methods were employed, and parallel experiments made with the same quantity of urine in each case. In one method, that of Liebig, the urine is fused with potassium hydroxide and nitrate; in the second, that of Carius, the urine is heated with fuming nitric acid in a sealed tube; in the third method, the one now proposed, 10 c.c. of urine is treated with 15 c.c. of fuming nitric acid in the cold. The first and second methods give approximately the same results, and are usually somewhat higher than the results obtained by the third method, which is regarded as the best.

W. D. H.

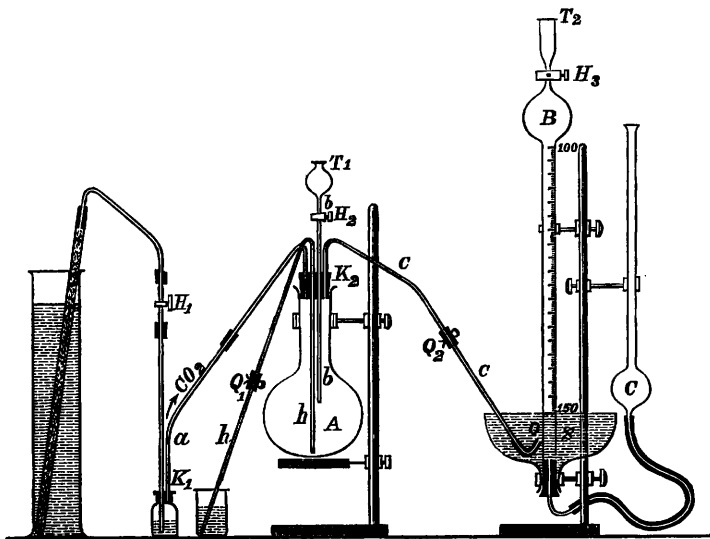
**Kjeldahl's Process of Estimating Nitrogen in Foods.** By A. BÖMER (*Chem. Zeit.*, 1895, **19**, 166—167).—The author recommends boiling the sample with sulphuric acid and a little mercury in the same flask, which afterwards serves for the distillation. In the case of cotton-seed and similar meals, 10 hours' boiling is required to obtain all the nitrogen as ammonia.

When phosphoric anhydride is added, the action is complete in four hours.

L. DE K.

**Estimation of Nitric acid.** By RICHARD BERGER (*Chem. Zeit.*, 1895, **19**, 305—306).—The process is based on the well-known conversion of nitric acid into nitric oxide. The following reagents, free from air, are required:—Hydrochloric acid of sp. gr. = 1.09; concentrated solution of ferrous sulphate; sulphuric acid of sp. gr. = 1.75, and aqueous potash of sp. gr. = 1.16. The chief part of the apparatus is the 200—250 c.c. Flask A which contains a few platinum cuttings, and in the 20-mm. wide neck of which a quadruply perforated indiarubber cork, K<sub>2</sub> is fitted. This is connected with the carbonic anhydride delivery tube *a*, the syphon *h* with pinchcock Q<sub>1</sub>, the tube *b* with a tap H<sub>2</sub> and funnel T<sub>1</sub>, and, lastly, with the tube *c*, having a pinchcock Q<sub>2</sub> and ending in a bend O, which is covered with a piece of indiarubber. It is important that the taps H<sub>1</sub>, H<sub>2</sub>, and H<sub>3</sub> shall turn

easily, and also that the tubes *a* and *c* shall not protrude from the bottom of the corks  $K_1$  and  $K_2$ .



The air from the apparatus is first displaced by a current of carbonic anhydride and of water vapour which is generated in A;  $H_1$  and  $Q_2$  being opened,  $H_2$  and  $Q_1$  closed. The parts of *b* and *h* which are not traversed by the gas are filled with water, *b* from  $T_1$ , by opening and then closing  $H_2$ ; *h*, by opening  $Q_1$ , at the same time closing  $Q_2$ . In the trough S is poured some water free from air, and the burette B is filled by opening  $H_3$  and then lifting the pipette C; the curved end of the tube *c* is then inserted into the opening O of the burette, which must be at a height of about 30 mm. from the bottom. As soon as the gas is completely absorbed by aqueous potash which is admitted from  $T_2$  by opening  $H_3$ , the source of heat from the flask is removed, the latter is emptied by opening  $Q_1$ , the syphon being, however, left filled.  $Q_2$  and  $H_1$  are also closed.

*Estimation of Nitre.*—After the apparatus is freed from air, the flask is charged by means of *b*, first with 10 c.c. of iron solution, then 25 c.c. of nitrate solution containing about 0.5 gram of solid matter, then again 10 c.c. of iron solution, followed by 25 c.c. of sulphuric acid, and finally once more 5 c.c. of iron sulphate. After shaking, the tap  $H_1$  is permanently, but not fully, opened. After a while warming is resorted to,  $Q_2$  is opened, and the heat so regulated that the bulk of the nitric oxide passes off in about five minutes. The gas collecting in the burette is freed from carbonic anhydride by admitting from time to time aqueous potash from  $T_2$ . When the iron solution has turned pure yellow, the flame is removed,  $Q_2$  and  $H_1$  are closed, and a few more cubic centimetres of iron solution are admitted into A, the mixture being again boiled for five minutes; a rapid stream of carbonic anhydride is passed at the same time so as to ensure the com-

plete expulsion of the nitric oxide. The burette is now placed in a cylinder filled with water free from air, and the gas is measured with the usual precautions.

By closing  $Q_2$  and emptying the flask by opening  $Q_1$  and closing  $H_1$ , the apparatus is at once ready for a second experiment. The process is, of course, applicable to sulphuric acid mixed, or contaminated, with nitric acid. The test analyses prove the great accuracy of the process.

L. DE K.

**Eggertz's Phosphorus Test.** By HANNS V. JÜPTNER (*Chem. Centr.*, 1894, ii, 449—450; from *Österr. Ung. Zeit. f. Berg. u. Huttenroesen*, **42**, 361—366).—The author gives the following modification of Eggertz's process, working without a centrifugal apparatus. 0.882 gram of the sample is dissolved in hot hydrochloric acid, oxidised with potassium permanganate, and any manganic dioxide dissolved by means of a few grains of oxalic acid. The liquid is then heated to  $40^\circ$ , mixed with 50 c.c. of molybdate solution, thoroughly shaken, and allowed to subside for a few hours. After syphoning off the clear supernatant fluid, the precipitate is transferred to the measuring tube, which is then placed in a shaking apparatus constructed on the principle of a stamping mill, which will cause the precipitate to be compressed. The author states that the results are very trustworthy when the precipitate looks a pure deep yellow and when its volume is nearly the average. If the sample is rich in silicon, this should be first removed; if very poor in phosphorus, a larger quantity should be weighed out. Admixture of arsenic is not to be feared if the temperature during the precipitation does not exceed  $40$ — $45^\circ$ .

L. DE K.

**Correct Estimation of Phosphorus in Iron and Steel.** By LIEBRICH (*Chem. Centr.*, 1895, i, 234; from *Stahl u. Eisen*, 1894, 1028—1029).—0.5—5 grams of the sample is dissolved in nitric acid (1.2 sp. gr.) and evaporated to dryness to render silica insoluble. The residue is dissolved in hydrochloric acid, diluted with water, and the metals precipitated by adding ammonia and ammonium sulphide. After warming, the liquid is filtered and the precipitate washed with hot dilute ammonium sulphide. The filtrate is mixed with a little magnesia mixture and then evaporated to dryness in a platinum dish. The residue is calcined to expel ammoniacal salts, then dissolved in hydrochloric acid, and the phosphoric acid precipitated as triple phosphate by adding ammonia. If arsenic or antimony is suspected, the acid solution is first freed from these metals by means of hydrogen sulphide. The results obtained by the author's process correspond with those got by the molybdate method.

L. DE K.

**Estimation of Phosphoric acid with Molybdate.** By JOSEPH HANAMANN (*Chem. Zeit.*, 1895, **19**, 553—554).—The author prepares his molybdate solution by dissolving 100 grams of molybdic acid in 1 litre of 10 per cent. ammonia and pouring this into 1.5 litre of nitric acid of sp. gr. 1.246. The precipitate which forms in the cold is washed with acid ammonium nitrate and nitric acid, and collected



on a Schleicher filter. It is then transferred to a platinum crucible and ignited, heating to actual redness being avoided, until it is uniformly blue-black. The paper is burnt separately. The ignited compound contains 4.018 per cent. of phosphoric anhydride. L. DE K.

**Estimation of small quantities of Arsenic.** By ADOLPHE CARNOT (*Compt. rend.*, 1895, **121**, 20—22).—The arsenic is precipitated as sulphide, converted into arsenic acid, and weighed as bismuth arsenate, which, when dried at  $110^{\circ}$ , has the composition  $2\text{BiAsO}_4 + \text{H}_2\text{O}$ . The precipitate of arsenic sulphide, mixed with more or less sulphur, is treated with warm ammonia solution, and the filtered liquid is mixed with excess of silver nitrate solution and heated for a short time. If silver nitrate solution no longer produces a precipitate, a small quantity of hydrogen peroxide solution is added and the liquid is heated at about  $100^{\circ}$  until all the ammonia is expelled. It is then slightly acidified with nitric acid, filtered, and mixed with excess of bismuth nitrate solution. An excess of ammonia is next added, the liquid boiled for a short time, the clear liquid decanted through a weighed filter, and the precipitate boiled with a mixture of nitric acid of sp. gr. 1.33 with an equal volume of water. The heavy, crystalline, insoluble precipitate is collected on a weighed filter, washed with dilute nitric acid (1:15) and finally with water, and dried at  $110^{\circ}$ .

Experiments with 10 c.c. of liquid containing 0.002976 gram of arsenic gave  $\pm 0.2$  milligram as the greatest error, the usual error being not more than 0.05 milligram. C. H. B.

**Titration of Arsenious acid by Permanganate.** By LUDWIG VANINO (*Zeit. anal. Chem.*, 1895, **34**, 426—431).—In spite of the brown coloration obtained when permanganate is added to a solution of arsenious acid, a very accurate titration can be obtained by working in a solution acidified with sulphuric acid and warmed to  $70^{\circ}$ , and taking as the end of the titration the point at which the mixture assumes a persistent, reddish-violet colour. It is, however, far more convenient to add a measured excess of permanganate (whether in the cold or at  $70^{\circ}$  is not indicated), and titrate the excess with a solution of hydrogen peroxide until the liquid becomes colourless, the end being quite sharp, and the results practically identical with those obtained by iodine titration. M. J. S.

**Estimation of Carbon in Iron.** By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1895, i, 134; from *Stahl u. Eisen*, 1894, 1029).—Three grams of steel borings is mixed with 10 grams of a mixture of three parts of lead powder and one part of copper powder and introduced into a porcelain boat, which is then put into a combustion tube. It is advisable to rest the boat on some asbestos. In front is placed a 10–20-cm. layer of copper oxide, and the combustion is then made, as usual, in a current of pure oxygen. The operation lasts about 45 minutes, the lead and copper serving as indirect oxidisers.

L. DE K.

**Analysis of Liquefied Carbonic Anhydride.** By LEO GRÜNHUT (*Chem. Zeit.*, 19, 1895, 505, 555).—In testing liquid carbonic anhydride, it is not sufficient to make an ultimate analysis of the gas which escapes on opening the tap of the bomb, as such an analysis is nearly always satisfactory, but the author advises examining the contents of the bomb after all the gas has escaped. In several cases, a quantity of discoloured liquid was found, chiefly consisting of glycerol, iron oxide, and organic matter of unpleasant odour. L. DE K.

**Potassium Tetroxalate for Titrating Alkalis.** By ARTHUR BORNTÄGER (*Zeit. anal. Chem.*, 1895, 34, 431—432).—The researches of Wells, Hinman, and Frear confirm the suspicion expressed by the author when advocating the use of potassium hydrogen tartrate for the above purpose, that potassium tetroxalate is difficult to prepare pure, is liable to effloresce when hydrated, and is hygroscopic when dehydrated. M. J. S.

**Estimation of Alkalinity in Raw Sugars.** By M. NEVOLE (*Chem. Centr.*, 1894, ii, 456; from *Österr. Ung. Zeit. Zucker. Ind. u. Landw.*, 1894, 3).—The author recommends Poupé's process, which involves the use of perfectly neutral litmus. This indicator is preferable to rosolic acid, recommended by Sachs. L. DE K.

**Detection and Estimation of Sodium in Lithium Salts.** By ISAAC W. THOMSON (*Zeit. anal. Chem.*, 1895, 34, 451—452; from *Chemist and Druggist*, 36, 240).—Whilst one part of sodium chloride requires for solution 600 parts of strong hydrochloric acid, lithium chloride is freely soluble. That a method of estimation depending on this fact can give good results is shown by the following experiment. Ten grams of lithium carbonate mixed with 2 per cent. of sodium carbonate were made up with water to 100 c.c., boiled, cooled, and made up to the original volume. Fifty c.c. of the filtrate was evaporated to dryness, and the residue treated with 15 c.c. of strong hydrochloric acid saturated with sodium chloride. After cooling, the chloride was thrown on a filter, washed first with 10 c.c. of the same liquid and then with pure hydrochloric acid. The residue, dissolved in water and evaporated to dryness, yielded 0.11 gram of sodium chloride, thus agreeing exactly with the 2 per cent. of sodium carbonate taken. The ether-alcohol method gives equally satisfactory results, but only in the absence of sulphates, whilst the above method is not affected by their presence. M. J. S.

**Separation of Mercury from the Metals of the Arsenic and Copper Groups.** By CARL V. USLAR (*Zeit. anal. Chem.*, 1895, 34, 391—413).—The method of Polstorff and Bülow (*Abstr.*, 1891, 1292) fails to separate mercury from cadmium or tin. That of H. Rose (precipitation of the mercury as mercurous chloride by phosphorous acid) has been found in some cases to give a deficiency in the quantity of mercury found. The author has submitted this method to a more minute examination, and finds that the mercury can be completely precipitated from a solution containing all the metals of

the above groups with the exception of tin, as the chlorides of this metal dissolve mercurous chloride. From copper, cadmium, arsenic, and antimony, the separation is complete, but in the case of bismuth or lead, traces are precipitated with the mercurous chloride, and a further separation by Polstorff's method is required. Except in the case of bismuth, when the addition of nitric acid must be avoided, the precipitation is best performed in a solution strongly acidified with nitric acid (25 c.c. of a 25 per cent. acid to 150 c.c. of the solution), since under these circumstances, as also in solutions only feebly acidified with hydrochloric acid, no reduction to metallic mercury ensues, whereas in solutions containing much hydrochloric acid a partial reduction of the mercurous chloride takes place, and a loss of mercury by volatilisation is possible. The solution is heated to 40—45°, 5 c.c. of a 20 per cent. solution of phosphorous acid for each decigram of mercuric chloride present is then added, and the mixture is kept at 40° for 5—6 hours. The precipitated mercurous chloride is washed with dilute acid (hydrochloric or nitric according to circumstances) and the filtrate again warmed with phosphorous acid for a few hours. The precipitate is then dissolved by hydrochloric acid and potassium chlorate, and the mercury precipitated by hydrogen sulphide; the precipitate is then purified if necessary by Polstorff's method (solution in a mixture of potassium sulphide and hydroxide, and reprecipitation from the filtered solution by ammonium chloride), and the sulphide once more dissolved by hydrochloric acid and chlorate; after the chlorine has been expelled by warming, the mercury is finally precipitated by hydrogen sulphide (with Polstorff's precautions, see *Arch. Pharm.*, **229**, 294) and dried on a weighed filter.

M. J. S.

**Estimation of Aluminium in Phosphates.** By HENRI LASNE (*Compt. rend.*, 1895, **121**, 63—66).—The mineral should be treated with hydrochloric acid, and the solution evaporated to dryness: in contact with the residue in order to decompose the fluorides and make the silica completely insoluble, since both would interfere with the determination. The residue is redissolved in the smallest possible quantity of hydrochloric acid and the solution diluted with 20 times its volume of water.

Aluminium phosphate is distinctly soluble in dilute acetic acid, but is insoluble in water containing ammonium chloride and a very slight excess of free ammonia. Ammonium thiosulphate readily precipitates the phosphate in a granular form, but the composition of the precipitate varies with that of the liquid in which it is produced. If, however, ammonium phosphate is added to a solution in such quantity that the liquid contains an excess of from 0.6 to 1.0 gram of phosphoric anhydride per litre, the composition of the precipitate corresponds exactly with normal aluminium phosphate.

Sodium hydroxide dissolves aluminium hydroxide in presence of an excess of phosphoric acid, whilst calcium, magnesium, iron, and manganese are precipitated. An excess of phosphoric acid is necessary in order to prevent the formation of a calcium aluminate, which is not decomposed by sodium hydroxide. Care must be taken that sodium carbonate is not formed during the washing of the precipitate.

The feebly acid solution of 1.25 gram of the phosphate free from silica is mixed with excess of sodium hydroxide free from silica and alumina, and sufficient sodium phosphate to provide an excess of phosphoric acid, and heated at  $100^{\circ}$  in a nickel dish for about an hour. The volume of the liquid is then made up to 250 c.c., and 0.5 c.c. is added to correct for the volume of the precipitate. The liquid is filtered, and 200 c.c., corresponding with 1 gram of the phosphate, is used for subsequent operations; this is acidified, and mixed with ammonium chloride and a slight excess of ammonia. The precipitate thus formed is drained, and redissolved in hot dilute hydrochloric acid, the solution being afterwards mixed with 3.5 c.c. of an ammonium phosphate solution (1 : 100), very nearly neutralised with ammonia, and diluted to about 250 c.c. 1.5 grams of ammonium thiosulphate is then added, the liquid boiled for half an hour, mixed with a few drops of a saturated solution of ammonium acetate, and again boiled for 10 minutes. The precipitate is washed with hot water, and heated with a blowpipe flame for 15 minutes.

C. H. B.

**Detection of Iron in Commercial Copper Sulphate.** By GIOACHINO GRIGGI (*Zeit. anal. Chem.*, 1895, **34**, 450; from *Boll. chim. farm.* through *Zeit. allgem. Oesterr. Apothekervereins*, **47**, 863).—Five c.c. of the aqueous solution (1 : 5) is covered in a test-tube with 5 c.c. of an ethereal solution of salicylic acid (1 : 10). The contact layer acquires a violet colour, the depth of colour depending on the proportion of iron present.

M. J. S.

**Colorimetric Assay of Cobalt Ores.** By KNIEDER (*Chem. Centr.*, 1894, ii, 452; from *Rev. Minera*, 1893, 398).—Twelve 200 c.c. flasks of the same calibre are selected. Eleven of them are filled with solutions of cobaltous chloride of increasing strength, varying from 0.1 to 2 grams of the crystallised salt. Twenty-five grams of the powdered ore is dissolved in a sufficiency of hydrochloric acid, the solution is diluted to 750 c.c., neutralised with chalk, and then diluted to 1 litre. Two hundred c.c. of the filtrate is now compared in the 12th 200 c.c. flask with the standard samples. If the ore is ferruginous or contains copper, the colour caused by these metals should be destroyed by adding sulphurous acid; presence of nickel renders the process useless.

L. DE K.

**Volumetric Estimation of Nickel.** By THOMAS MOORE (*Chem. News*, 1895, **72**, 92—93).—The process is based on the one used by Campbell and Andrews (this vol., ii, 421), but the author gives an important modification: 20—25 grams of pure potassium cyanide is dissolved in a litre of water, and to this is added a solution of about 0.25 gram of silver nitrate. If this solution is added to an ammoniacal solution of nickel containing a little potassium iodide, a precipitate of silver iodide is formed, and this will increase until all the nickel has been converted into double cyanide, when an excess of the cyanide will cause the liquid to clear again.

The value of the cyanide is ascertained, as usual, on a nickel solution of known strength. Cobalt, if present in the sample, will count

as nickel. The employment of organic acids or sodium pyrophosphate in case iron or zinc is present dispenses with their tedious separation, which is a matter of considerable importance in the assay of nickel matte or German silver.

L. DE K.

**The Estimation of Molybdenum.** By CARL FRIEDHEIM and HANS EULER (*Ber.*, 1895, **28**, 2061—2067).—Molybdenum sulphide can readily be converted into molybdic anhydride without loss, when it is washed free from sulphuric acid, dried at  $100^{\circ}$ , and then ignited along with the filter paper, at first in a covered crucible and then exposed to the air. The ignited mass is treated with ammonia, filtered from any unburnt carbon, evaporated to dryness, and carefully heated.

The method proposed by Mauro and Danesi for the volumetric estimation of molybdenum, which depends on the reduction of the anhydride by hydriodic acid, may be conveniently carried out by distilling the molybdate, which is to be analysed, with potassium iodide and hydrochloric acid and collecting the liberated iodine in potassium iodide solution. The amount of iodine set free is then estimated with thiosulphate solution.

A. H.

**Volumetric Estimation of Molybdic and Vanadic Anhydrides in the same Solution.** By CARL FRIEDHEIM and HANS EULER (*Ber.*, 1895, **28**, 2067—2073; compare foregoing abstract).—Holverschreit (*Dissertation, Berlin*, 1890) has shown that when vanadic anhydride is distilled with fuming hydrochloric acid and potassium bromide, it is quantitatively reduced to vanadium tetroxide. On the other hand, vanadic anhydride is completely converted into the trioxide when it is distilled with hydrochloric acid, a little phosphoric acid, and potassium iodide.

These reactions, together with the reaction of molybdic anhydride described in the preceding abstract, render it possible to estimate vanadic and molybdic anhydrides volumetrically in the same solution. For this purpose, the mixture is first distilled with fuming hydrochloric acid and potassium bromide, by which the vanadic anhydride is reduced to vanadium tetroxide with liberation of bromine; this is collected in potassium iodide solution, and the liberated iodine estimated by sodium thiosulphate solution. The residue in the retort is then distilled with hydrochloric acid, a little syrupy phosphoric acid, and potassium iodide. In this way the vanadium tetroxide is further reduced to the trioxide, an amount of iodine being liberated which is equal to that set free in the previous reduction of the pentoxide to tetroxide, whilst the molybdic anhydride is converted into the oxide  $\text{Mo}_2\text{O}_5$ .

The reactions are as follows. (1)  $\text{V}_2\text{O}_5 + 2\text{HBr} = \text{V}_2\text{O}_4 + \text{H}_2\text{O} + \text{Br}_2$ . (2) (a)  $\text{V}_2\text{O}_4 + 2\text{HI} = \text{V}_2\text{O}_3 + \text{H}_2\text{O} + \text{I}_2$ ; (b)  $2\text{MoO}_3 + 2\text{HI} = \text{Mo}_2\text{O}_5 + \text{H}_2\text{O} + \text{I}_2$ .

The amount of iodine corresponding with the molybdic anhydride present is therefore found by subtracting from the total iodine liberated during the second distillation, an amount equal to that liberated during the first.

The authors hope to extend this method to the determination of other oxides.

A. H.

**Estimation of Uranium in Earths containing Phosphoric and Arsenic Acids.** By C. REMIGIUS FRESSENIUS and E. HINTZ (*Zeit. anal. Chem.*, 1895, **34**, 437—439).—Separation by the ordinary methods presents many difficulties. The feebly acid (hydrochloric) solution from which silica has been removed is precipitated with an excess of potassium ferrocyanide, and then saturated with sodium chloride. This addition causes the precipitate to settle rapidly, and enables it to be filtered and washed easily. The precipitate is thoroughly washed with sodium chloride solution, and then decomposed in the cold with dilute potash. After partial washing by decantation the hydroxides are rinsed on to a filter with water containing ammonium chloride and ammonia, and washed with the same solution until free from ferrocyanide. The oxides, which are now free from phosphoric and arsenic acids, are dissolved in hydrochloric acid, the solution is nearly neutralised with ammonia, mixed with an excess of ammonium carbonate, and digested for some time in the cold to precipitate the iron. The filtrate is heated to remove the greater part of the ammonium carbonate, acidified with hydrochloric acid, and treated with hydrogen sulphide to remove copper. From the filtrate, the uranium is precipitated by ammonia and weighed either as uranoso-uranic oxide, or, after ignition in hydrogen, as uranous oxide. A test analysis gave a perfectly satisfactory result.

M. J. S.

**Separation of Bismuth from Lead.** By OLAV STEEN (*Zeit. angew. Chem.*, 1895, 530—535).—The author has investigated 12 published methods for the separation of bismuth from lead, and tabulated the results. Three processes only can be recommended: Rose's process, in which the lead is estimated as sulphate and the bismuth as oxychloride; Lowe's process, in which the bismuth is separated as oxynitrate and the lead as sulphide or sulphate; Jannasch's method, in which the bismuth is volatilised as bismuth bromide by heating the mixed sulphides in a stream of bromine vapour mixed with air.

L. DE K.

**Separation of Gold and Silver from Iron and Steel.** By HENRY N. WARREN (*Chem. News*, 1895, **72**, 100—101).—In order to test some bars of iron of 1-in. circumference for gold and silver, 4 lbs. of the sample was attached to the positive pole of a battery of 3 volts 40 ampères, a carbon negative electrode being used; dilute sulphuric acid was employed by the author as a solvent. The mass having disappeared save a thin wire of iron, this carboniferous residue was dried, intimately mixed with chemically pure litharge, and reduced in the usual way. The silver button was afterwards examined for gold by parting.

Calculating to percentages of the carboniferous residue, Swedish iron yielded 0·8 per cent., Low Moor iron 0·1 per cent., and Danne-

mora iron 0.064 per cent. of silver; this was found to contain traces of gold.

L. DE K.

**Gasometric Estimation of Glycerol.** By FRIEDRICH GANTTER (*Zeit. anal. Chem.*, 1895, **34**, 421—426).—Glycerol can be very conveniently estimated by the use of the author's gas volumeter (Abstr., 1894, ii, 26) to measure the volume of carbonic anhydride evolved when the glycerol is oxidised by potassium dichromate and sulphuric acid. In the flask are placed 3 grams of solid potassium dichromate and 5—10 c.c. of the glycerol solution containing not more than 0.3 gram of glycerol, and in the pipette 10 c.c. of sulphuric acid consisting of 2 vols. of the concentrated acid diluted with 1 vol. of water. The greater part of the dichromate is now dissolved by gently warming, and the sulphuric acid is then admitted a drop at a time. When all the acid has been run in, and the action slackens, the mixture is heated to boiling and kept in ebullition for 15 minutes. The special laboratory vessel employed for nitric acid estimations, with an empty absorption tube between the flask and the pipette should be used.

Employing this method, the author has studied the behaviour of aqueous and alcoholic solutions of glycerol when evaporated, and finds that no loss of glycerol occurs during the evaporation to dryness on the water-bath, but commences when the residue is heated at 100° after the complete evaporation of the solvent. An estimation of the glycerol in a fat (by saponification with strong soda, decomposition of the soap, filtration from the fatty acid, and assay of the aqueous filtrate) can be completed in 80 minutes.

M. J. S.

**Detection of Small Quantities of Sugar in Urine.** By HERMANN FOCKE (*Chem. Centr.*, 1894, ii, 453; from *Apoth. Zeit.*, **9**, 559).—Ten grams of the sample is boiled with 5 grams of copper sulphate solution (1—9); after cooling, the liquid is filtered and mixed with 2 grams of solution of sodium carbonate (1—9) and, after settling, again filtered. Of the urine thus purified, a few drops are added to a hot Fehling's solution diluted with an equal bulk of water, and the whole is boiled; if sugar is present, a characteristic red precipitate will be obtained. If the amount of sugar is below 0.05 per cent., the whole of the filtrate should be mixed with some more copper solution, excess of alkaline solution of Rochelle salt added, and the mixture boiled.

L. DE K.

**Testing Urine for Acetone.** By C. GULDENSTEEDEN EGELING (*Chem. Centr.*, 1894, ii, 457—448; from *Nederl. Tydschr. Pharm. &c.*, **6**, 217—218).—Diabetic urine is generally tested for acetone by Legal's reaction; addition of sodium nitroprusside, aqueous soda and then acetic acid, which produces a carmine-red colour. According to Salkowski, this test is not decisive, as aldehyde, for instance, also gives the colour. A more trustworthy test is given by Le Nobel, namely, addition of sodium nitroprusside and ammonia, when a splendid violet colour is gradually developed. The reaction is also given by acetoacetic acid, but as this always accompanies acetone and is itself

readily split up into acetone and carbonic anhydride, the author thinks that Le Nobel's test is the best.

L. DE K.

**Estimation of Hydrocyanic Acid.** By CARL GLÜCKSMANN (*Chem. Centr.*, 1895, i, 134; from *Pharm. Post.*, 1895, 525—527).—The author recommends the following modification of Denigès' process which is useful when the presence of ammonia is suspected. Fifty c.c. of the sample, cherry-laurel water for instance, is diluted with an equal bulk of distilled water, and, if turbid, cleared by adding alcohol. 0.2 gram of potassium iodide and 5 c.c. of ammonia are added, and the hydrocyanic acid rapidly titrated by running in N/10 silver nitrate solution until the liquid gets turbid.

L. DE K.

**Estimation of the Volatile Acids in Wines.** By E. BURCKER (*Compt. rend.*, 1895, 120, 1223—1225).—The author has investigated the accuracy of his method of estimating the volatile acids in wine by distilling in a current of steam and titrating the distillate with decinormal sodium hydroxide solution, using phenolphthaleïn as indicator. Experiments were made with solutions of various acids and hydrogen salts usually present in wines, about 10 per cent. of alcohol by volume being added to the solutions. The results show that non-volatile acids, whether present in the free state or as salts, exert no appreciable influence on the acidity of the distillate. The acidity is due mainly to acetic acid, and any of the latter which is present in the form of calcium salt, &c., is completely liberated by adding a small quantity of succinic or tartaric acid or potassium hydrogen tartrate.

The method of distillation in steam gives results comparable with those obtained by determining the total acidity, and the residual acidity after evaporation in a vacuum.

The maximum acidity in French wines is equivalent to 0.70 gram of sulphuric acid per litre, whilst in Algerian and Tunisian wines it may be as high as 1.60 gram.

C. H. B.

**Estimation of Uric acid and Xanthine Compounds in Urine.** By ERNST SALKOWSKI (*Chem. Centr.*, 1894, ii, 456; from *Centr. Med. Wiss.*, 1894, 514—515).—The uric acid is precipitated from 500—1000 c.c. of urine by means of ammoniacal solution of silver nitrate, after the phosphatic matter has been removed by means of magnesium mixture. The precipitate, suspended in water, is decomposed with hydrogen sulphide, and the filtrate evaporated to dryness; the residue is then treated for 24 hours with a little water containing 2—3 per cent. of sulphuric acid, which dissolves the xanthine compounds, and leaves the uric acid as it is practically insoluble. It is not advisable to try and remove any dissolved uric acid by means nitric acid, as this also partly destroys the xanthine compounds, but the latter may be reprecipitated by means of ammoniacal silver nitrate, and estimated from the amount of metallic silver in the precipitate. The author found the quantity to be about 8—10 per cent. of the uric acid. These xanthine substances are not true xanthenes, but resemble hypoxanthine.

L. DE K.



**Estimation in Butter of the Fatty Acids Soluble in Water containing Sulphuric acid.** By ALEXANDER ZEGA (*Chem. Zeit.*, 1895, 19, 504—505).—2—2.5 grams of butter fat is weighed into a 200 c.c. calibrated flask, 2 c.c. of aqueous potash is added, and then 10 c.c. of alcohol, the flask being heated on the top of the water bath until saponification seems complete. The flask is now placed in boiling water for 20 minutes to expel the bulk of the spirit, and the soap is dissolved in 50—70 c.c. of hot water; after cooling, the solution is diluted to the mark, 2 c.c. of sulphuric acid, strong enough to leave an excess of 0.6 c.c. of acid, is added, the mixture well shaken, and filtered. Fifty c.c. of the filtrate is titrated with N/10 soda, using methyl-orange as indicator; another 50 c.c. is then titrated with the aid of phenolphthaleïn. The number of c.c. of soda of the first titration deducted from the second experiment gives the soda representing the soluble fatty acids. One gram of pure butter fat consumes about 5.8 c.c. of N/10 alkali. L. DE K.

**Centrifugal Estimation of Fat in Milk.** By JOSEF ZEHENTER (*Chem. Centr.*, 1894, ii, 458; *Program Oberrealschule, Innsbruck* 1893—94).—The author has come to the conclusion that the estimation of fat in milk by means of the centrifugal machines and the processes of both Babcock and Gerber leaves nothing to be desired, as regards accuracy. As regards cream, the results are not quite so accurate, but still satisfactory when the sample is weighed out instead of being measured. L. DE K.

**Milk Analysis.** By ERNST BECKMANN (*Chem. Centr.*, 1895, i, 239; from *Milch Zeit.*, 23, 702—703).—*Estimation of Fat.*—Twenty-five c.c. (or grams) of the sample is put into a stoppered glass cylinder, diluted with an equal volume of water, and shaken with 2.5—5 c.c. of basic lead acetate; solution of sodium carbonate is then added to promote precipitation. The deposit is collected, and put back into the cylinder, together with some glass bulbs of 3 mm. in diameter; agitation with ether now removes the fat completely without producing an emulsion. The filter is washed with ether, which may then be used to extract the precipitate. The process gives accurate results with all kinds of milk. Sour milk is best precipitated with ammoniacal basic lead acetate.

*Freezing Point.*—This is dependent on the amount of water, but independent of the amount of fat. Genuine milk has a low, constant, freezing point,  $-0.54^{\circ}$  to  $-0.58^{\circ}$ , average  $-0.554^{\circ}$ . The experiment is made by placing the sample in a mixture of ice and salt, actively stirring with a delicate thermometer. As soon as the temperature goes down to  $-1^{\circ}$  or  $-2^{\circ}$ , there is again a sudden rise, and it then remains very constant for some time. This gives the freezing point, which, in careful hands, will tell the presence of 10 per cent. of water. L. DE K.

**Analysis of Cheese.** By M. KÜHN (*Chem. Zeit.*, 1895, 19, 554; 601—602; 648—649).—The chief mode of adulterating cheese is by adding margarine to the skim-milk from which the cheese is prepared.

In testing such cheese, it is important to extract the whole of the fat before submitting it to analysis. The mere taking of its specific gravity is nowadays not sufficient to form an opinion, but the extracted fat should be tested by the Reichert-Wollny or, better still, by the Köttstorfer process. The refractometer may also give useful indications, and has the advantage of requiring but little fat. When using it, the fat should be perfectly free from ether. Fats which are somewhat decomposed have a tendency to give too high a refraction.

L. DE K.

**Estimation of Fat in Animal Organs.** By C. DORMEYER (*Pflüger's Archiv*, 1895, **61**, 341—342).—For the extraction of fat from animal organs, Soxhlet's apparatus was found to give imperfect results, for, after 100 hours' extraction with ether, in spite of the finely divided state of the tissue, fat still remained undissolved. It is recommended that the tissue should be subjected to artificial gastric digestion before extraction; the powdered flesh was then found to yield an additional 0.75 per cent. of fat.

W. D. H.

**Detection of Earth-nut Oil.** By HANS KREIS (*Chem. Zeit.*, **19**, 1895, 451—452).—The author recommends the following modification of Rénard's process:—The fatty acids from 20 grams of the sample are dissolved in 300 c.c. of ether, and slowly mixed with 150 c.c. of alcohol containing 15 grams of lead acetate; the lead oleate remains almost entirely in solution, and the deposit consists of the lead salts of the solid fatty acids. After washing these with ether, they are boiled with 250 c.c. of 5 per cent. hydrochloric acid, until the fatty acids have quite melted, washed a few times with boiling water, to remove the lead chloride, and, after cooling, the cake is dried between blotting paper, and dissolved in 100 c.c. of 90 per cent. alcohol with the aid of a gentle heat. On cooling, any arachidic acid will slowly crystallise out, and may afterwards be recognized by its melting point ( $74^{\circ}$ ). Its weight multiplied by 110 gives the approximate percentage of arachis oil in the sample.

L. DE K.

**Essential Oils.** By SCHIMMEL and Co. (*Zeit. anal. Chem.*, 1895, **34**, 480—483).—In consequence of partial oxidation, the essential oils from dried plants differ somewhat in specific gravity and optical rotation from those obtained from fresh plants. The latter are also generally paler in colour, purer in odour, and freer from resin than the former. The constituents of bay oil (*Oleum myricæ*) are eugenol, "myrcen" ( $C_{10}H_{16}$  ? myrtene), chavicol ( $C_9H_{10}O$ ), methyleugenol, methylchavicol, phellandrene, and geranaldehyde ( $C_{10}H_{16}O$ ). The sp. gr. varies from 0.965 to 0.985. The phenols, which amount to 60—65 per cent., can be approximately estimated by shaking 10 c.c. of the oil with strong potash in a flask with narrow graduated neck, and driving the undissolved (non-phenolic) residue into the neck by gradual addition of water. Adulteration with turpentine oil can be detected by examining for pinene. From 10 c.c. of the oil, 1 c.c. is slowly distilled off and mixed with 1 c.c. of amylic nitrate and 2 c.c. of glacial acetic acid. Then, whilst shaking and keeping cold, a

mixture of equal parts of hydrochloric acid and glacial acetic acid is added as long as a blue coloration is produced. In presence of pinene, a white precipitate of pinene nitrosochloride is formed.

The sp. gr. of citron oil at  $10^{\circ}$  is 0.8625, and the rotation  $[\alpha]_D = \frac{100\alpha}{l\delta} = +74^{\circ}10'$ . For a rise of  $1^{\circ}$  up to  $20^{\circ}$ , the sp. gr. diminishes by 0.00082, and the rotation (in a 100 mm. tube) by  $0^{\circ}9'$ . From  $20^{\circ}$ — $30^{\circ}$ , the changes are 0.00068 and  $0^{\circ}7'8''$  per degree. For orange oil, the values at  $10^{\circ}$  are: 0.8550 and  $+116^{\circ}36'$ , and up to  $20^{\circ}$  the diminution per degree 0.00081 and  $0^{\circ}14'5''$ ; and, from  $20^{\circ}$  to  $30^{\circ}$ , 0.00073 and  $0^{\circ}13'2''$ .

To detect geraniol in essential oils, when the proportion exceeds 25 per cent., the dry oil is intimately mixed with an equal weight of dry powdered calcium chloride, and the mixture kept in a desiccator at  $-4^{\circ}$  or  $-5^{\circ}$  for 12—16 hours. The soft mass is rubbed up with dry benzene, ether, or light petroleum, and the liquid portion removed by a suction filter. The calcium chloride compound of geraniol is then treated with water, and the oil separated, washed, and distilled, when geraniol passes over at  $228$ — $230^{\circ}$ . M. J. S.

**Estimation of Urea in Urine.** By A. KOSSEL and H. SCHMIED (*Chem. Centr.*, 1895, i, 236—237; from *Du Bois-Raymond Arch.*, 1894, 552—553).—Ten c.c. of urine mixed with a little barium carbonate is heated in a sealed tube at  $180^{\circ}$  for an hour. The contents are transferred to a distilling flask, barium hydroxide is added, and the distillate collected in an absorption apparatus containing N/10 acid. Experiments with solutions of urea of known strength proved the accuracy of the authors' process, which is not influenced by the presence of uric or hippuric acid. L. DE K.

**Estimation of Nicotine and Ammonia in Tobacco.** By VIKTOR VEDRÖDI (*Zeit. anal. Chem.*, 1895, **34**, 413—420).—The author now recognises that the error in Kissling's method which he attributed to the passing over of ammonia along with the nicotine (*Abstr.*, 1893, ii, 504) is due to soda carried over by the steam, and therefore recommends that the addition of the 50 c.c. of 4 per cent. soda solution to the light petroleum (not ethylic ether as Kissling appears to have used) extract (see *Abstr.*, 1882, 1005) should be omitted, since the whole of the nicotine in the petroleum extract is already in the free state, and that the distillation should be carried on without the use of a steam current, except that when the contents of the retort have been evaporated almost to dryness a current of steam should be admitted to sweep into the receiver the last traces of nicotine. Before beginning the distillation, 100 c.c. of water is added to the petroleum extract. About one-fifth of the nicotine comes over with the petroleum, the remainder with the aqueous distillate. To titrate the petroleum distillate, 50 c.c. of water is added, then litmus, and of the standard acid a few drops at a time until the water below the petroleum remains coloured violet even after shaking vigorously.

Experiments made with tobacco powder, which had been first freed from nicotine and ammonia by making alkaline with alcoholic

soda, extracting with light petroleum and drying, and had then been mixed with known amounts of nicotine, with or without ammonium chloride, gave fairly correct yields, the greatest error amounting to a loss of 6 per cent. of the nicotine taken, and the estimation being unaffected by the presence of the ammonia. The distillation of the tobacco itself with soda (10 c.c. of the 6 per cent. alcoholic soda, and 100 c.c. of water, to 20 grams of tobacco) gives both the nicotine and ammonia, so that the ammonia is known from the difference between the two titrations.

The paper contains some unexplained arithmetical discrepancies.

M. J. S.

### **Estimation of Theobromine in Cocoa-nibs and in Cocoa.**

By ALBERT HILGER and A. EMINGER (*Chem. Centr.*, 1894, ii, 462; from *Forschungsber. Lebensm.*, 1, 292).—Ten grams of the powdered sample is digested with 150 grams of light petroleum for 12 hours, the insoluble portion is dried, and 5 grams of it is boiled with water containing 3 per cent. of sulphuric acid for fully half an hour, using a reflux condenser. The mixture is then neutralised with barium carbonate, some sand added, and the whole evaporated to dryness. The mass is extracted with 100 grams of chloroform, and the residue left on evaporating the latter, is extracted with carbon tetrachloride to remove impurities such as fat and caffeine. The theobromine is further purified by dissolving, in water, filtering, and evaporating the solution.

L. DE K.

**Detection and Estimation of Strychnine in Corpses.** By ALLERTON S. CUSHMAN (*Chem. Centr.*, 1894, ii, 461; from *Trans. Acad. Sci., St. Louis*, 6, 17).—In cases of strychnine poisoning, the alkaloid should be quantitatively estimated, but as the author has found that a good deal of it is destroyed by the usual process of heating the impure chloroform extract with strong sulphuric acid to destroy fatty and colouring matters, he prefers to treat the alcoholic extract with water and a few drops of acetic acid, and then to repeatedly extract the aqueous solution with ethylic acetate. The purified liquid is then rendered alkaline with sodium carbonate, and again agitated with ethylic acetate, which now dissolves the strychnine. The residue left on evaporating the solvent is dissolved in water and a little acetic acid, and purified by agitating with a mixture of ether and chloroform. The liquid is then rendered alkaline with ammonia and again agitated with the said mixture; the alkaloid will then be left in a very pure state on evaporating the mixture. In two experiments, 86.2—87.8 per cent. of added strychnine was respectively recovered.

L. DE K.

**Detection and Estimation of Albumin in Urine.** By E. RIEGLER (*Zeit. anal. Chem.*, 1895, 34, 485—486; from *Wiener Klin. Wochenschs.*, 1894, No. 52).—To 4—5 c.c. of the urine there is added 10 drops of a 10 per cent. solution of calcium  $\beta$ -naphthol- $\alpha$ -sulphonate (asaprol), previously mixed with one-tenth of its volume of concentrated hydrochloric acid. Albumin, albumoses, and peptones, when amounting to only 0.01 per cent., are precipitated. On

warming, the albumoses and peptones redissolve, the albumin remaining insoluble. If filtered hot, the albumose and peptone precipitate reappears on cooling the filtrate. M. J. S.

**Estimation of the Nitrogenous Constituents of Meat Extract and Commercial Peptones.** By ALBERT STUTZER (*Zeit. anal. Chem.*, 1895, 34, 372—380).—This article consists chiefly of modifications of the methods previously described (Abstr., 1893, 146). Contrary to the statement then made, gelatin-peptone is found to be insoluble in absolute alcohol. The viscosimetric method of estimating gelatin being inconvenient when only a small quantity of substance is available, the alcohol method of Kemmerich and Denaeyer (see Abstr., 1894, ii, 150) has been tried, and found to return 95—98 per cent. of the gelatin taken. It is to be noted that meat extracts contain ammonia, but in what state of combination is uncertain. It can be determined by distilling with barium carbonate.

The course of the analysis is as follows:—Unchanged muscular fibres should be sought for with the microscope, and, if found, a weighed quantity of the substance is extracted with cold water, and the nitrogen determined in the insoluble matter, the filtrate being acidified with acetic acid and boiled for estimation of albumin. For the estimation of the water, the substance is first weighed into a tinfoil capsule and there dissolved in a little hot water; a weighed quantity of ignited, long-fibred asbestos, sufficient to absorb all the liquid, is then added, and the whole dried in the water bath. The residue serves for the gelatin estimation; for this purpose, the capsule and contents are cut up and washed four times with absolute alcohol, extracted with water, to which 1/10 of its volume of alcohol has been added, at a temperature not exceeding 5°, and finally washed with the same until the washings are colourless. The filter and contents are then boiled with water, and in the solution obtained the gelatin is estimated (from a nitrogen determination). The precipitations with ammonium sulphate are carried on as in the former paper, but instead of estimating the adhering ammonium sulphate by a sulphuric acid determination, the ammonia is expelled by evaporating the solution with excess of barium carbonate. M. J. S.

**Analysis of Meat Extracts and Peptones.** By ALBERT STUTZER (*Zeit. angew. Chem.*, 1895, 529).—The author calls attention to the fact that most of the analyses of these articles have been made by methods, the scientific value of which is rather doubtful.

An analysis is given of a Liebig-Kemmerich's meat peptone, showing the amount of the various nitrogenous substances and mineral salts present in it. The analysis has been made by the author's method (preceding abstract). L. DE K.

**Analysis of Gastric Juice.** By J. WINTER (*Bull. Soc. Chim.*, 1895 [3], 13, 433—441).—The fixed chlorides are estimated in the ash obtained on heating the residue from the evaporation of the gastric juice (5 c.c.) over a naked flame for five minutes; the result is constant for the same sample. The slight loss of chlorine during the incinera-

tion is probably due to a cause other than mere volatilisation, for when the ash is taken to dryness again with hydrochloric acid, the resulting gain is found to vary with the stage of digestion at which the sample was taken.

In determining the free and organic hydrogen chloride, several portions of the juice are evaporated and dried respectively at 100°, 110°, 120°, and 135°, and a further portion is incinerated; the chlorine is then estimated in the original liquid and in each dried portion, and the loss of hydrogen chloride at each stage of drying calculated; the sum of the losses is always practically equal to the acidity of the juice.

The author designates as free hydrogen chloride that portion which is volatilised at 100°, and, as the organic acid, that portion which remains at that temperature; in both forms, it probably exists in complex, unstable, albuminoid combination. JN. W

**Estimation of Dry Matter in Peat.** By H. PUCHNER (*Landw. Versuchs-Stat.*, 1895, **46**, 221—231).—A number of peaty soils were heated at 105° for 14 days, being weighed every 24 hours. The soils first lost in weight continuously; then the loss was very slow, the soils sometimes gaining slightly for a day or two owing to oxidation. It was quite impossible to obtain a constant weight. It is probable that oxygen is taken up by the organic matter, and is then partly eliminated as water; there was also a loss of nitrogen. There was more increase in weight when the soils were cooled over sulphuric acid than when calcium chloride was employed. When the soils were dried in a vacuum over sulphuric acid and over phosphoric anhydride, constant weights were obtained after a good many days; but the two sets of results did not always agree. The only trustworthy method seems to be keeping the soil in a vacuum over phosphoric anhydride. N. H. J. M.

## ERRATA.

## VOL. LVIII (ABSTR., 1890).

Page	Line	
43	9*	for " $\text{C}_6\text{H}_4\text{Me} \begin{smallmatrix} \text{CPh} \\ \text{CO-} \end{smallmatrix} \text{NO}$ ," read " $\text{C}_6\text{H}_4\text{Me-N} \begin{smallmatrix} \text{CPh} \\ \text{CO-} \end{smallmatrix} \text{NO}$ ."
721	8*	„ " $\text{NH}_2\text{-NMe}$ " read " $\text{NH}_2\text{-NOMe}$ ."
970	17*	„ " $\text{Ph}\cdot\underset{\text{O}}{\underset{ }{\text{C}}}\cdot\text{NH}$ " „ " $\text{Ph}\cdot\underset{\text{O}}{\underset{ }{\text{CH}}}\cdot\text{NH}$ ."
1000	12*	„ " $\text{CPh}\cdot\underset{\text{CO-O}}{\text{CH}} \text{>} \text{C}\cdot\text{C}_4\text{NH}_4$ " read " $\text{CPh}_2\cdot\underset{\text{CO-O}}{\text{CH}} \text{>} \text{C}\cdot\text{C}_4\text{NH}_4$ ."
1440	9*	„ " $\text{O} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CH}\cdot\text{N} \end{smallmatrix}$ " read " $\text{O} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CH}\cdot\text{N} \end{smallmatrix}$ ."

## VOL. LX (ABSTR., 1891).

57	10*	for "azoinide" read "azoimide."
442	3*	„ "ketoximes" read "aldoximes."
653	14*	after "bromonitropropane" insert "and zinc-methyl."
1008	4*	for "yield three" read "yield two."

## VOL. LXIV (ABSTR., 1893).

## PART II.

536	17*	for "hydrargilite" read "hydrargillite."
577	24	„ " $2\text{PO}_4\text{CaH}_2 + 3\text{H}_2\text{O}$ " read " $2\text{PO}_4\text{CaH} + 3\text{H}_2\text{O}$ ."

## VOL. LXVI (ABSTR., 1894).

## PART I.

438	5*	for " $\text{C}_3\text{H}_5\text{O}_2(\text{CH}_2)_2\text{OH}$ " read " $\text{C}_3\text{H}_5\text{O}_2(\text{CH}_2)\cdot\text{OH}$ ."
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## PART II.

283	13	for "A shows three points of transformation" read "A, like carburetted iron, shows three points of transformation at which there is thermal change."
290	3*	„ "observed" read "obscured."
291	5 & 6	„ " <i>Sapindus</i> , <i>Saponaria</i> , and <i>Esculentus</i> " read " <i>Sapindus saponaria</i> and <i>S. esculentus</i> ."
291	6	„ " <i>Amara</i> " read " <i>P. amara</i> ."
496	17, col. ii,	for "Beneville, J. S. de" read "Benneville, J. S. de."

## VOL. LXVIII (ABSTR., 1895).

## PART I.

Page	Line	
5	16*	for "ECKENSTEIN" read "EKENSTEIN."
40	13	„ "CPh·C(NO·CO·C <sub>7</sub> H <sub>7</sub> )·OEt" read "OEt·CPh·N·O·CO·C <sub>7</sub> H <sub>7</sub> ."
53	13	„ "converted into" read "obtained from."
92	4	„ "WILLSTÄTER" read "WILLSTATTER."
116	21*	„ "CRÄMER" read "CRAMER."
281	12	„ "CESARIS" „ "CESARIS."
334	bottom	„ "ethylic para- $\phi$ -diketosebate" read "ethylic $\gamma\phi$ -diketosebate."
345	19*	„ "sulphuric acid" read "nitric acid."
345	18*	„ "zinc dust and glacial acetic acid" read "alcoholic ammonium sulphide."
368	4	} for "paratoluidineacetoparatoluidide" read "paratolylimidoacetyl-paratoluidide."
525	18*	
382	5, 7	„ "Citron oil" read "Lemon oil."
428	11*	„ "Dihydrocampholenolactone" read "Hydroxydihydrocampholenolactone."
451	23*	„ "d-Phenylacetic" read "d-Phenylchloracetic."
525	9*	„ "Paratoluidineacetic acid" read "Paratolylimidoacetic acid."
603	12*	„ "OSCAR" read "OSKAR."
659	6*	„ "N <sub>2</sub> Ph·CH(CN)·COOEt" read "C <sub>6</sub> H <sub>4</sub> Br·N <sub>2</sub> ·CH(CN)·COOEt."

## PART II.

20	2, 14*, 1*	} for "Zeit. Kryst. Min., 33" read "Zeit. Kryst. Min., 23."
21	8, 13*	
22	7*	
23	13*	
20	15	for "E. K. DUMBLE" read "E. J. DUMBLE."
21	19	„ "titaniferous" read "titanic."
22	16	„ "1" read "50-64."
22	18	„ "occurs" read "occurs at the latter locality."
76	20	„ "3RO, SiO <sub>2</sub> , R <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> " read "3(RO, SiO <sub>2</sub> ), R <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> ."
101	3, 23*	„ "LOUGUININE" read "LUGININ."
120	14*, 12*	„ "pancreatic" „ "gastric."
129	13*	„ "stability" read "lability."
172	19*	„ "Laurium" „ "Laurion."
267	18*, 16*	„ "spark discharge" read "silent discharge."
332	15*	„ "Diazobenzenesulphonic" read "Paradiazobenzenesulphonic."
335	21*	„ "GERARD" read "GÉRARD."
402	17, 6*	„ "triolite" read "troilite."
403	15*	„ "starch" „ "starch paste."
408	21	„ "of Folia Bucco" read "in Folia Bucco (Buchu leaves)."
505	15	„ "rhodocerosite" read "rhodochrosite."
541	4	„ "citron oil" read "lemon oil."
576	30, col. ii, for	"Manassee" read "Manasse."
576	3*, col. ii, „	"Jeans Charles Gallissard" read "Jean Charles Galissard."
579	14*, col. i }	for "Morell" read "Morrell."
587	10, col. ii }	

\* From bottom.